

# THE FAINT YOUNG SUN PROBLEM

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For more than four decades, scientists have been trying to find an answer to one of the most fundamental questions in paleoclimatology, the ‘faint young Sun problem’. For the early Earth, models of stellar evolution predict a solar energy input to the climate system which is about 25% lower than today. This would result in a completely frozen world over the first two billion years in the history of our planet, if all other parameters controlling Earth’s climate had been the same. Yet there is ample evidence for the presence of liquid surface water and even life in the Archean (3.8 to 2.5 billion years before present), so some effect (or effects) must have been compensating for the faint young Sun. A wide range of possible solutions have been suggested and explored during the last four decades, with most studies focussing

on higher concentrations of atmospheric greenhouse gases like carbon dioxide, methane or ammonia. All of these solutions present considerable difficulties, however, so the faint young Sun problem cannot be regarded as solved. Here I review research on the subject, including the latest suggestions for solutions of the faint young Sun problem and recent geochemical constraints on the composition of Earth’s early atmosphere. Furthermore, I will outline the most promising directions for future research. In particular I would argue that both improved geochemical constraints on the state of the Archean climate system and numerical experiments with state-of-the-art climate models are required to finally assess what kept the oceans on the Archean Earth from freezing over completely.

## 1. INTRODUCTION

The faint young Sun problem for Earth’s early climate has been briefly reviewed a few times in the past, for example in the general context of climate change on geological timescales [Crowley, 1983; Barron, 1984], the formation and early history of Earth [Zahnle *et al.*, 2007], the evolution of Earth’s atmosphere and climate [Pollack, 1991; Kasting, 1993; Shaw, 2008; Nisbet and Fowler, 2011], life on the early Earth [Nisbet and Sleep, 2001], evolution of the terrestrial planets and considerations of planetary habitability [Pollack, 1979; Rampino and Caldeira, 1994; Kasting and Catling, 2003] or the evolution of the Sun [Kasting and Grinspoon, 1991; Güdel, 2007]. The more comprehensive reviews of this topic are somewhat dated by now, however, and most look at the issue from the point of view of the global energy balance without exploring important internal aspects of the climate system like the transport of heat.

This paper presents a new and detailed review of the faint young Sun problem and is organized as follows. Section 2 describes the evidence for a faint young Sun and for the existence of liquid water on early Earth. Section 3 explores in what ways the

faint young Sun problem could be solved in principle before the options are discussed in detail in the following sections. Section 4 looks at modifications of the standard solar model, in particular the possibility of a strong mass-loss of the young Sun. The most likely solution of the faint young Sun problem in terms of an enhanced greenhouse effect is discussed in Section 5, the main Section of this review paper. Then the effects of clouds (Section 6) and differences in rotation rate and continental configuration (Section 7) will be explored, before the review is concluded by a summary and suggestions for future research in Section 8.

## 2. THE FAINT YOUNG SUN PROBLEM

In this Section, the faint young Sun problem is introduced, beginning with a discussion of the evolution of the Sun on long timescales.

### 2.1. A Fainter Sun in the Past

By the 1950s, stellar astrophysicists had worked out the physical principles governing the structure and evolution of stars [Kippenhahn and Weigert, 1994]. This allowed the construction of theoretical models for the stellar interior and the evolutionary changes occurring during the lifetime of a star. Applying these principles to the Sun, it became clear that the luminosity of the Sun had to change over time, with the young Sun being considerably less

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luminous than today [Hoyle, 1958; Schwarzschild, 1958].

According to standard solar models, when nuclear fusion ignited in the core of the Sun at the time of its arrival on what is called the zero-age main sequence (ZAMS) 4.57 Ga (1 Ga =  $10^9$  years ago), the bolometric luminosity of the Sun (the solar luminosity integrated over all wavelengths) was about 30% lower as compared to the present epoch [Newman and Rood, 1977]. The long-term evolution of the bolometric solar luminosity  $L(t)$  as a function of time  $t$  can be approximated by a simple formula [Gough, 1981]

$$\frac{L(t)}{L_{\odot}} = \frac{1}{1 + \frac{2}{5} \left(1 - \frac{t}{t_{\odot}}\right)}, \quad (1)$$

where  $L_{\odot} = 3.85 \times 10^{26}$  W is the present-day solar luminosity and  $t_{\odot} = 4.57$  Gyr (1 Gyr =  $10^9$  years) is the age of the Sun. Except for the first  $\sim 0.2$  Gyr in the life of the young Sun, this approximation agrees very well with the time evolution calculated with more recent standard solar models [e.g., Bahcall et al., 2001], see the comparison in Figure 1.

Note that solar models had been under intense scrutiny for a long time in the context of the “solar neutrino problem”, an apparent deficiency of neutrinos observed in terrestrial neutrino detectors [Haxton, 1995] which is now considered to be resolved by a modification of the standard model of particle physics [Mohapatra and Smirnov, 2006] rather than to be an indication of problems with solar models. Furthermore, the time evolution of the Sun’s luminosity has been shown to be a very robust feature of solar models [Newman and Rood, 1977; Bahcall et al., 2001]. Thus it appears highly unlikely that the prediction of low luminosity for the early Sun is due to fundamental problems with solar models. (Slightly modified solar models involving a larger mass loss in the past will be discussed in Section 4.)

In a way the robustness of the luminosity evolution of stellar models is not surprising, since the gradual rise in solar luminosity is a simple physical consequence of the way the Sun generates energy by nuclear fusion of hydrogen to helium in its core. Over time, Helium nuclei accumulate, increasing the mean molecular weight within the core. For a stable, spherical distribution of mass twice the total kinetic energy is equal to the absolute value of the potential energy. According to this virial theorem, the Sun’s core contracts and heats up to keep the star stable, resulting in a higher energy conversion rate and hence a higher luminosity. There seems no possibility for escape [Gough, 1981]: “The gradual increase in luminosity during

the core hydrogen burning phase of evolution of a star is an inevitable consequence of Newtonian physics and the functional dependence of the thermonuclear reaction rates on density, temperature and composition.”

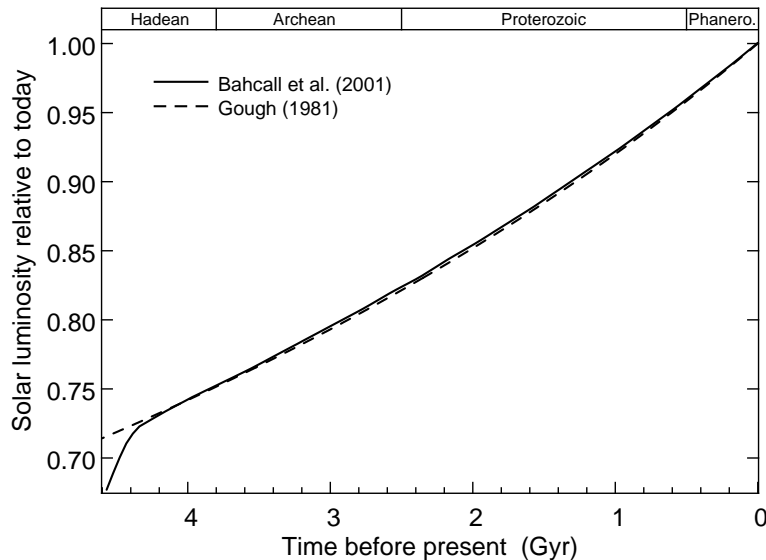
In addition to this slow evolution of the bolometric solar luminosity over timescales of  $\sim 10^9$  yr, the Sun exhibits variability on shorter timescales of up to  $\sim 10^3$  yr [Fröhlich and Lean, 2004]. This variability in solar radiation is a manifestation of changes in its magnetic activity related to the solar magnetic field created by a magnetohydrodynamic dynamo within the Sun [Weiss and Tobias, 2000]. The bolometric solar luminosity is dominated by radiation in the visible spectral range originating from the Sun’s lower atmosphere which shows very little variation with solar activity [Fröhlich and Lean, 2004]. For the present-day Sun, for example, total solar irradiance varies by only  $\simeq 0.1\%$  over the 11-year sunspot cycle [Gray et al., 2010].

The Sun’s ultraviolet radiation, on the other hand, is predominantly emitted by the hotter upper layers of the solar atmosphere which are subject to much larger variability [Lean, 1987; Fröhlich and Lean, 2004]. Solar variability (and thus ultraviolet luminosity) was higher in the past due to a steady decrease in magnetic activity over time caused by the gradual slowing of the Sun’s rotation which ultimately drives the magnetohydrodynamic dynamo [Zahnle and Walker, 1982; Dorren and Guinan, 1994; Güdel, 2007]. From observations of young stars similar to the Sun one can infer a decrease in rotation rate  $\Omega_{\odot}$  of the Sun with time  $t$  which follows a power law

$$\Omega_{\odot} \propto t^{-0.6} \quad (2)$$

[Güdel, 2007]. For the same reason, the solar wind was stronger for the young Sun, with consequences for the early Earth’s magnetosphere and the loss of volatiles and water from the early atmosphere [Sternborg et al., 2011], especially considering the fact that the strength of Earth’s magnetic field was estimated to be  $\sim 50 - 70\%$  of the present-day field strength 3.4 – 3.45 Ga [Tarduno et al., 2010]. The effects of these changes in ultraviolet radiation and solar wind will be briefly discussed later on.

Coming back to the lower bolometric luminosity of the Sun, an estimate of the amount of radiative forcing of the climate system this reduction corresponds to is given by  $\Delta F = \Delta S_0(1 - A)/4$  (the change in incoming solar radiation corrected for geometry and Earth’s albedo  $A$ ). Using the present-day solar constant  $S_0 \simeq 1361$  W m $^{-2}$  [Kopp and Lean, 2011] and Earth’s current albedo  $A \simeq 0.3$  yields values of  $\Delta F \approx 60$  W m $^{-2}$  and  $\Delta F \approx 40$  W m $^{-2}$  at times 3.8 Ga and 2.5 Ga, respectively.



**Figure 1.** Evolution of solar luminosity over the four geologic eons for the standard solar model described in *Bahcall et al.* [2001, *solid line*] and according to the approximation formula [*Gough*, 1981, *dashed line*] given in equation (1).

For comparison, the net anthropogenic radiative forcing in 2005 is estimated to be  $\simeq 1.6 \text{ W m}^{-2}$  [*Forster et al.*, 2007].

Solar physicists speculated early on that this large reduction of the incoming solar radiation might have had consequences for the evolution of Earth’s climate [*Schwarzschild*, 1958]: “Can this change in the brightness of the sun have had some geophysical or geological consequences that might be detectable?”

## 2.2. Evidence for Liquid Water on Early Earth

A few years later, the possible consequences of these astrophysical findings of a faint young Sun on the climate of Earth were first discussed by *Ringwood* [1961], who pointed out that “[o]ther factors being equal, [...] the surface of the earth during the period between its birth, 4.5 billion years ago, and 3 billion years ago, would have passed through an intense ice age.”

A significant reduction in solar energy input can result in dramatic effects for the Earth’s climate due to the ice-albedo feedback: Decreasing temperatures result in larger areas covered in ice which has a large albedo and thus reflects more radiation back into space, further enhancing the cooling. Climate models show the importance of this ice-albedo feedback for the Earth’s global energy balance: Once a critical luminosity threshold is reached, this results in run-away glaciation and completely ice-covered oceans, a “snowball Earth” [*Kirschvink*, 1992] state (see also Figure 8 and the discussion in Section 7). It should be noted that a recent modeling study suggests a third stable state in which a narrow strip in the tropics remains

free of ice due to the combined effects of the lower albedo of snow-free sea ice and the reduced cloud cover in this region [*Abbot et al.*, 2011].

While earlier models placed the critical luminosity threshold at 2 – 5% below the present-day value for modern continental configuration [*Budyko*, 1969; *Sellers*, 1969; *Gérard et al.*, 1992], later studies with more sophisticated models found values of 10 – 15% and up to 18% for global ocean conditions [*Jenkins*, 1993; *Longdoz and François*, 1997]. Differences in critical luminosity between energy-balance models can be attributed to the sensitivity of the ice line to the parametrization of meridional heat transport [*Held and Suarez*, 1975; *Lindzen and Farrell*, 1977; *Ikeda and Tajika*, 1999], to geography [*Crowley and Baum*, 1993] and to the question whether the climate model is coupled to a dynamic ice-sheet model or not [*Hyde et al.*, 2000]. Furthermore, the position of the ice line in simulations with comprehensive general circulation models is strongly influenced by ocean dynamics [*Poulsen et al.*, 2001].

Once snowball Earth conditions are reached, it requires high concentrations of greenhouse gases in the atmosphere (for example from the gradual build-up of volcanic carbon dioxide in the atmosphere) to return to a warmer climate state due to the high reflectivity of the ice, although volcanic ash and material from meteorite impacts might lower the albedo and thus increase the absorption of solar radiation [*Schatten and Endal*, 1982].

Note that the oceans would not have been frozen completely (i.e., down to the ocean floor) because of the flow of geothermal heat from the Earth’s interior. For the case of a cold climate on early Earth, the thickness of the ice layer at the oceans’

surface has been estimated with a simple one-dimensional heat flow model to be a few hundred meters given the higher geothermal heat flux at that time [Bada *et al.*, 1994]. Models like this ignore the effects of ice dynamics, however.

Contrary to these expected climatic effects of the faint young Sun, however, there is ample evidence for the presence of liquid water at the surface of the young Earth during the Hadean and Archean eons. For the purpose of this review, the Hadean eon is defined to span the period from the Earth's formation 4.56 Ga to 3.8 Ga and the Archean eon is assumed to last from the end of the Hadean to 2.5 Ga. Note that the Hadean is not officially defined and that there is no agreement about the Hadean-Archean boundary which is frequently set at 4.0 Ga [see, e.g., Zahnle *et al.*, 2007; Goldblatt *et al.*, 2010, for discussions]. It appears logical, however, to define the beginning of the Archean at the end of the period of intense impacts from space known as the 'Late Heavy Bombardment' [Tera *et al.*, 1974; Wetherill, 1975; Hartmann *et al.*, 2000; Kring and Cohen, 2002] occurring  $\sim 4.0 - 3.8$  Ga, although the exact end of that period is not resolved in the geological record. Irrespective of these matters of definition, it is important to realize that the Archean, the main focus of this review, spans a very long period of time in the history of Earth.

Tentative evidence for liquid water on the early Earth can be found in the Hadean. No rocks are known from the Hadean due to the exponential decrease of preservation with age, yet some information on the surface conditions during those earlier times can be derived from the mineral zircon ( $\text{ZrSiO}_4$ ) preserved from the Hadean in younger rocks [Harrison, 2009]. Indeed, zircon grains may provide evidence for liquid water even before the Archean, as early as 4.2 Ga [Mojzsis *et al.*, 2001; Wilde *et al.*, 2001; Valley *et al.*, 2002; Harrison, 2009].

Note, however, that the environment in which this Hadean ocean existed was considerably different from the Archean [for a review of the following outline of events see, e.g., Zahnle *et al.*, 2007]. The Earth was formed by gravitational accretion of smaller bodies (planetesimals) formed in the nebula surrounding the young Sun. The large impact forming the Moon occurred after 50 Myr towards the end of the accretion period. After this event, Earth was enshrouded in rock vapor for 1000 yr. A strong greenhouse effect (caused by large amounts of carbon dioxide and water vapor degassing from the mantle) and tidal heating by the still tightly-orbiting Moon kept the surface covered by a magma ocean for a few million years after the Moon-forming impact. Then the crust so-

lidified and a hot water ocean with temperatures of  $\sim 500$  K formed under a dense atmosphere containing  $\sim 100$  bar of carbon dioxide. The carbon dioxide in the atmosphere was then subducted into the mantle over timescales of  $10^7 - 8$  yr, before the Late Heavy Bombardment ( $\sim 4.0 - 3.8$  Ga) set the stage for the Archean eon. It is thus clear that the processes resulting in a liquid-water ocean in the Hadean are considerably different from the Archean, so they will not be discussed further in this review.

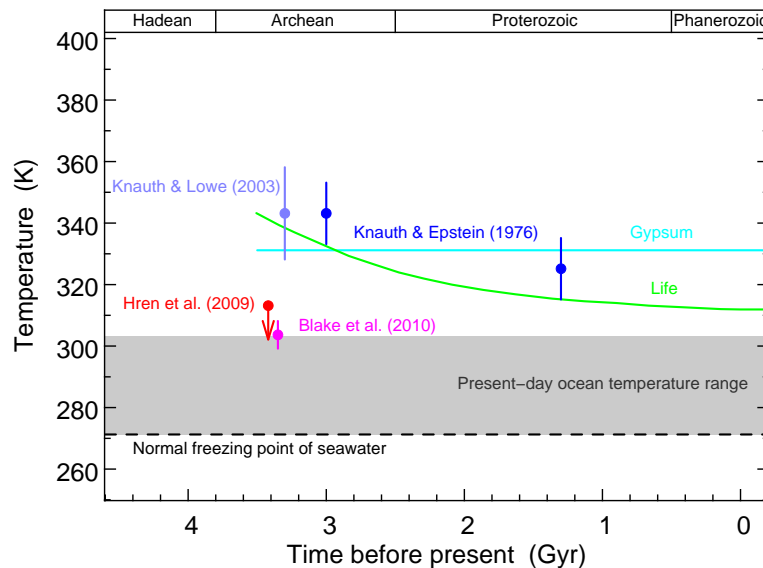
Geologic evidence for liquid surface water during the Archean is mostly based on sedimentary rock laid down in a variety of aqueous conditions up to 3.5 Ga and possibly as early as 3.8 Ga, and there is no evidence for wide-spread glaciations during the entire Archean [see Lowe 1980; Walker 1982; Walker *et al.* 1983; for more recent overviews of Archean geology in general see, e.g., Fowler *et al.* 2002; Eriksson *et al.* 2004; Benn *et al.* 2006]. Tell-tale signs of liquid water include pillow lavas which are formed when lava extrudes under water, ripple marks resulting from sediment deposition under the influence of waves, and mud cracks.

Furthermore, there is evidence for microbial life in the Archean derived from microfossils or stromatolites/microbial mats in rocks of ages between 2.5 and 3.5 Gyr [Barghoorn and Schopf, 1966; Altermann and Kazmierczak, 2003; Schopf, 2006]. Although all life on Earth is based on the existence of liquid water [e.g., Pace, 2001], the mere existence of life is only a poor constraint on ice cover. The early evidence of photosynthetic cyanobacteria and stromatolites, however, constitutes further evidence for an early Earth not permanently covered by ice (or at least for continuously ice-free regions in the oceans). One could, in principle, imagine photosynthetic life under a thin ice cover in the tropics of a snowball Earth as postulated by McKay [2000] and investigated in Pollard and Kasting [2005, 2006]. Later studies have indicated, however, that ice cover would have been too thick even in the tropics [Warren *et al.*, 2002; Goodman, 2006; Warren and Brandt, 2006], making such a scenario unlikely.

In summary, there are multiple lines of independent evidence suggesting the existence of liquid water on Earth's surface during the Archean, when the Sun was considerably fainter than today.

### 2.3. Temperatures during the Archean

It is one of the key characteristics of water that it remains liquid over a rather wide range of temperatures, so the question arises of how warm the Archean climate actually was. The constraints on and estimates of Archean ocean temperatures discussed below are summarized in Figure 2.



**Figure 2.** Constraints on ocean temperatures during the Archean. The existence of diverse life since about 3.5 Gyr and the typical ranges of temperature tolerance of living organisms suggests the upper limit indicated by the *green line* [Walker, 1982]. Evaporate minerals are present since about 3.5 Gyr, and the fact that many were initially deposited as gypsum sets an upper limit at 58°C (*cyan line*) [Holland, 1978]. The comparatively high (but controversial, see the text for discussion) temperatures derived from oxygen isotope ratios in cherts are shown in *blue* [Knauth and Epstein, 1976; Knauth and Lowe, 2003]. More recent estimates based on a combination of oxygen and hydrogen isotope ratios [Hren et al., 2009] and the oxygen isotope composition of phosphates [Blake et al., 2010] are shown in *red* and *magenta*, respectively. The range of present-day ocean temperatures is indicated in *gray* [Locarnini et al., 2010], the freezing point of seawater at normal pressure and for present-day salinity by the *dashed line*. Modified and updated after Walker [1982].

Upper limits to Archean climate temperatures can be mainly derived from two lines of argument. First, evaporite minerals can be found in the geological record back to 3.5 Ga, and since many of these were originally precipitated in the form of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), which is converted to anhydrite ( $\text{CaSO}_4$ ) at temperatures above 58°C in pure water (and at lower temperatures in seawater), temperatures cannot have been higher than this value [Holland, 1978, 1984; Walker, 1982]. Secondly, the continued presence of life and the typical heat tolerance of living organisms can be used to estimate an upper limit in the range of 40 – 60°C [Walker, 1982].

In conflict with these upper limits from evaporites and the continued presence of life, low values of the  $\delta^{18}\text{O}$  isotope ratio in 3.5 to 3.0 Ga cherts were interpreted by some researchers as evidence of a hot climate with oceanic temperature of 55 – 85°C [Knauth and Epstein, 1976; Karhu and Epstein, 1986; Knauth and Lowe, 2003; Robert and Chausidon, 2006]. There is a lot of debate, however, about how strongly oxygen isotope ratios actually constrain temperatures. It has been argued, for example, that these data could reflect a low  $\delta^{18}\text{O}$  of ancient seawater rather than a hot climate [see e.g., Walker, 1982; Kasting and Ono, 2006; Kasting and Howard, 2006; Kasting et al., 2006; Jaffrés et al., 2007, for discussions]. An alternative expla-

nation for changes in isotope ratios during the Precambrian has been put forward by van den Boorn et al. [2007] who argue that the data might reflect more widespread hydrothermal activity on the ancient seafloor.

In light of this discussion there appears to be no strong argument in favor of a hot Archean climate. Indeed, a recent analysis combining oxygen and hydrogen isotope ratios indicates ocean temperatures below 40°C for a sample of 3.4 Ga old rock [Hren et al., 2009]. Blake et al. [2010] analyzed  $\delta^{18}\text{O}$  isotope compositions of phosphates in 3.2 – 3.5 Gyr-old sediments and interpreted the high  $\delta^{18}\text{O}$  found in their samples as being indicative of low oceanic temperatures in the range 26 – 35°C. These temperatures are close to the maximum of the annually averaged sea-surface temperature of about 30°C today [Locarnini et al., 2010].

Although the evidence appears to point towards a temperate Archean climate, the question of how warm the early Earth’s atmosphere was is certainly not quite settled yet. One further major problem is that oceanic temperatures are expected to strongly vary with latitude and depth. It is unknown, however, at what latitudes and depths the rocks were formed on which the temperature estimates discussed above are based. Notwithstanding these problems, the Archean climate was almost certainly warm enough to keep the ocean surface

from freezing completely despite the low solar luminosity.

#### 2.4. Why was the Early Earth not Frozen?

*Donn et al.* [1965] were, to my knowledge, the first to point out the apparent discrepancy between the low solar luminosity predicted for the young Sun and the evidence for liquid water on early Earth. Not believing in a strong greenhouse effect in the early atmosphere, they speculated that it could be used to put constraints on solar models and theories of continental formation, an idea that certainly appears rather optimistic from today's perspective.

As mentioned above, after the development of simple energy-balance climate models by the end of the 1960s scientists began to study the connection between a slight decrease in solar luminosity and glaciations on Earth [e.g., *Budyko*, 1969; *Sellers*, 1969], but the results had been discussed in the context of the Quaternary glaciation rather than the climate of early Earth. The predictions of solar models for a faint young Sun went not unnoticed in the planetary science community, however: *Polack* [1971] investigated the effect of the lower solar luminosity on the early atmosphere of Venus.

One year later, *Sagan and Mullen* [1972] explored the effects of the lower luminosity of the young Sun on the early Earth. *Sagan and Mullen* are usually credited as having discovered the faint young Sun problem. While this is not entirely true as the discussion above shows, they were certainly the first to make it known to a wider public and to suggest a solution in terms of an enhanced greenhouse effect. For their analysis, they used the fundamental equation for Earth's global energy balance (see equation (3) in Section 3), finding that global surface temperature should have remained below the freezing point of sea-water for the first two billion years of Earth's history with today's greenhouse gas concentrations and albedo (see Figure 3). These calculations neglected any feedback effects from water vapor and included only simplified representations of the ice-albedo feedback effect, however, so the problem was considered to be even more severe in reality.

This conundrum of liquid water in a climate powered by a feeble Sun has been termed the 'faint young Sun problem' [*Ulrich*, 1975], sometimes also the 'faint early Sun problem' or 'faint young Sun paradox'. It is only a paradox, of course, if the Sun indeed was much fainter in the early days of the solar system (alternative theories are discussed in Section 4), and if the parameters controlling the climate in the Archean were similar to today's values, an assumption which appears naive considering the profound changes Earth has experienced in

its long history. Indeed, changes in atmospheric concentrations of greenhouse gases are one of the possibilities to resolve the apparent inconsistency between the faint young Sun and the temperate climate on early Earth (see Section 5).

Note that there is also evidence for the presence of liquid water during several periods in the history of Mars, including at very early times [*Carr*, 1996]. The problem of keeping early Mars warm would be even more profound due to its larger distance from the Sun and considerably smaller mass, if there were indeed extended periods of warm climate on early Mars. The faint young Sun problem for Mars, however, will not be discussed in this review paper.

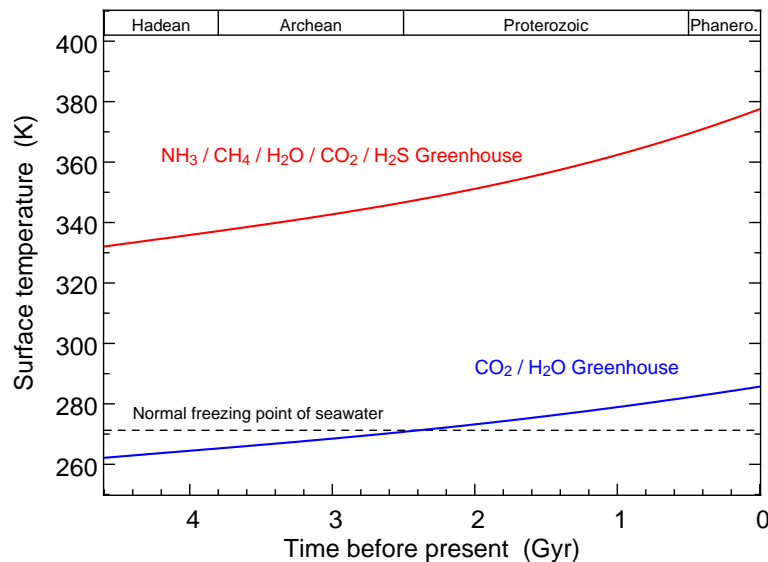
### 3. WARMING THE EARLY EARTH

Before discussing possible solutions to the faint young Sun problem in detail, it is helpful to ask which parameters govern the temperature of Earth's atmosphere. The mean surface temperature  $T_s$  of the atmosphere can be approximated by the following equation for the case of a gray atmosphere, where the infrared absorption by greenhouse gases is assumed to be independent of wavelength, [*Emden*, 1913; *Milne*, 1922; *Wildt*, 1966; *Stibbs*, 1971]:

$$T_s^4 = \frac{1}{\varepsilon\sigma} \frac{R^2}{4} \frac{L_\odot}{4\pi r^2} (1 - A) \left( 1 + \frac{3}{4}\tau^* \right) \quad (3)$$

The variables in this equation are the Earth's effective surface emissivity  $\varepsilon$ , the Stefan-Boltzmann constant  $\sigma$ , the Earth's radius  $R$ , the solar luminosity  $L_\odot$ , the average distance  $r$  between Sun and Earth, the albedo  $A$ , and the column infrared gray opacity  $\tau^*$  representing the warming effect of greenhouse gases.

Although solar energy is by far the most important source of energy for today's climate system, other sources of energy (like heat from Earth's interior, tidal energy from the gravitational interaction with the Sun and the Moon, or the energy released after impacts from space) could, in principle, provide additional heating to the early atmosphere. Today, the globally integrated heat loss from the Earth's interior (mostly originating from radioactive decay) amounts to less than  $5 \times 10^{13}$  W [*Polack et al.*, 1993; *Davies and Davies*, 2010]. Taking into account Earth's surface area of  $5.1 \times 10^{14}$  m<sup>2</sup>, this corresponds to  $\sim 0.1$  W m<sup>-2</sup>, more than three orders of magnitude smaller than the climate forcing due to solar irradiance of  $\simeq 240$  W m<sup>-2</sup> for the present-day solar constant (the solar irradiance at the top of the atmosphere) of 1361 W m<sup>-2</sup> [*Kopp and Lean*, 2011]. Total heat flow due to radioactive decay is estimated to be factors of  $\sim 3$  and  $\sim 2$



**Figure 3.** Average surface temperature evolution of Earth as a function of time given the changes in solar luminosity and assuming present-day concentrations of carbon dioxide and water vapor (*blue line*) according to *Sagan and Mullen* [1972]. The calculations follow equation (3) and assume a total pressure of 1 bar, an atmospheric composition constant with time and a fixed albedo of 0.35. Going into the past, the surface temperature drops below the normal freezing point of water  $\sim 2$  Ga in this model. The solution of the faint young Sun problem suggested by *Sagan and Mullen* [1972] in terms of greenhouse gas warming dominated by ammonia ( $\text{NH}_3$ , see Section 5.1) is shown as well (*red line*). In this scenario, volume mixing ratios  $10^{-5}$  of  $\text{NH}_3$ ,  $\text{CH}_4$  and  $\text{H}_2\text{S}$  have been added to the  $\text{CO}_2$ - $\text{H}_2\text{O}$  greenhouse. In terms of warming, ammonia is the dominant greenhouse gas in this case, Modified after *Sagan and Mullen* [1972].

higher than today for the early and late Archean, respectively [*Taylor and McLennan*, 2009]. Thus even on the early Earth, flows of internal heat are at least two orders of magnitude too small to compensate for the faint young Sun [*Endal and Schatten*, 1982].

Dissipation of tidal energy amounts to about  $3.5 \times 10^{12}$  W (or  $\sim 0.007$  W  $\text{m}^{-2}$ ) today [*Munk and Bills*, 2007], one order of magnitude smaller than the geothermal heat flux. During the Archean, tides were higher due to the smaller distance  $r_M$  to the Moon [*Walker and Zahnle*, 1986] which also influences the dissipation rate of tidal energy due to the changes in orbital period and day-length [*Zahnle and Walker*, 1987]. The tidal energy dissipation rate during the Archean can be estimated from the equations in *Munk* [1968] and the evolution of lunar distance [*Walker and Zahnle*, 1986] to be a factor of  $\sim 3$  higher because of these effects, yielding an energy flux of  $\sim 0.02$  W  $\text{m}^{-2}$ , again insufficient to provide enough energy to counteract the lower solar irradiation.

The energy deposited by impactors from space can be estimated by integrating the impact probability distribution [*Stuart and Binzel*, 2004] over all energies, yielding an insignificant contribution to the energy budget of about  $5 \times 10^8$  W (corresponding to only  $10^{-6}$  W  $\text{m}^{-2}$ ) for the recent geological history. Impacts were much more frequent

very early in Earth's history, but the frequency of major impacts from space had decreased dramatically with the end of the Late Heavy Bombardment ( $\sim 4.0$  to  $3.8$  Ga) already before the beginning of the Archean [*Tera et al.*, 1974; *Wetherill*, 1975; *Sleep et al.*, 1989; *Hartmann et al.*, 2000; *Kring and Cohen*, 2002], and was at most one order of magnitude higher than today after the Late Heavy Bombardment, too low to deliver significant amounts of energy globally [*Hartmann et al.*, 2000; *Valley et al.*, 2002]. Major impacts could result in occasional melting of frozen oceans during the Archean, however [*Bada et al.*, 1994]. Given the widespread evidence for liquid surface water during the Archean, episodic melting appears to be an unsatisfactory solution to the faint young Sun problem.

Values for the surface emissivity  $\varepsilon$  are very close to one and do not vary much between different surface types [e.g., *Wilber et al.*, 1999], so any variations in  $\varepsilon$  between four billion years ago and today are small and cannot contribute significantly to the solution of the faint young Sun problem. Furthermore, a long-term increase in Earth's orbital radius  $r$  since the Archean seems unlikely. While planetary migration through exchange of angular momentum is a widely discussed feature of current models for the formation phase of planetary systems, it is limited to the comparatively short formation time during which there is a protoplanetary



disk and planetesimals with which an exchange of angular momentum is possible [Papaloizou and Terquem, 2006].

Extremely speculative hypotheses like a potential variation of the gravitational constant with time avoiding a faint young Sun [Newman and Rood, 1977; Tomaschitz, 2005] appear unlikely and will not be discussed here.

In summary, a solution to the faint young Sun problem requires a higher solar luminosity  $L_{\odot}$  than predicted by standard solar models, a lower overall albedo  $A$  (and therefore increased absorption of solar radiation) or a significantly enhanced greenhouse effect, i.e., increased infrared opacity  $\tau^*$  (or a combination of these). All these have been suggested in the literature and will be discussed in the remainder of this review article.

#### 4. MODIFICATIONS OF THE STANDARD SOLAR MODEL

The faint young Sun problem originates from the fact that the standard solar model implies a considerably lower luminosity for the early Sun. If the solar luminosity were higher than predicted by the standard solar model, however, there might be no problem at all [Ulrich, 1975].

The steady increase in solar luminosity with time shown in Figure 1 is a fundamental corollary of the physical equations governing the structure of and energy conversion within stars (see Section 2.1). The only escape route appears to be a change in stellar mass, since the luminosity  $L$  of a star powered by nuclear fusion of hydrogen to helium in its core (so called main-sequence stars) steeply increases with its mass  $M$  according to

$$L \propto M^{\eta}, \text{ where } \eta \simeq 2 - 4 \quad (4)$$

[Kippenhahn and Weigert, 1994].  $\eta$  depends on the mass of the star; for stars like the Sun, a value of  $\eta \simeq 4$  is usually adopted. According to this mass-luminosity relation, a higher mass of the young Sun would therefore go hand in hand with a higher initial solar luminosity and would have the potential to avoid the faint young Sun problem. Indeed, a higher initial mass together with an enhanced mass loss of the early Sun has been suggested to avoid the faint young Sun problem [Boothroyd et al., 1991; Graedel et al., 1991].

The present-day Sun loses mass due to two processes. First, hydrogen is converted to helium in its core. The mass of the resulting helium nucleus is less than the total mass of the protons entering this fusion reaction, and the energy difference corresponding to this mass difference is emitted by the Sun. Secondly, mass is continuously transported

away from the Sun by the solar wind, a stream of charged particles (primarily electrons and protons) originating in the Sun's upper atmosphere.

The mass-loss rates due to nuclear fusion and the solar wind amount to  $\dot{M}_{\text{fusion}} \simeq 7 \times 10^{-14} M_{\odot} \text{ yr}^{-1}$  and  $\dot{M}_{\text{wind}} \simeq 2 \times 10^{-14} M_{\odot} \text{ yr}^{-1}$  [Wood, 2004], respectively, yielding a total mass loss of  $\dot{M} \simeq 1 \times 10^{-13} M_{\odot} \text{ yr}^{-1}$  for today's Sun ( $M_{\odot} \simeq 2 \times 10^{30} \text{ kg}$  denotes the present-day solar mass). Assuming that this mass-loss rate has not changed over the main-sequence lifetime of the Sun, this would result in a solar mass only 0.05% higher 4.57 Ga, yielding a negligible increase in luminosity according to equation (4).

The solar wind, however, is known to have been stronger for the young Sun because of the higher solar activity in the past (see Section 3). Depending on the assumed mass-loss history, a young Sun with an initial mass  $\sim 4\%$  higher than today would be bright enough to explain the presence of liquid water on Mars 3.8 Ga [Sackmann and Boothroyd, 2003], and an initial mass of  $\sim 6\%$  higher than today makes the Sun as bright as today 4.5 Ga, although the solar luminosity would still drop below today's levels during the Archean [Guzik et al., 1987; Sackmann and Boothroyd, 2003]. In addition to the direct increase in energy input due to the higher solar luminosity, Earth would also be closer to a more massive Sun on its elliptical orbit, further enhancing the warming effect, with the semi-major axis  $a(t)$  at time  $t$  inversely proportional to the solar mass  $M(t)$  [Whitmire et al., 1995]

$$a(t) \propto \frac{1}{M(t)}. \quad (5)$$

There are limits to the mass of the early Sun, however. A weak upper limit can be derived from the fact that at higher solar luminosities Earth would have run into a runaway greenhouse effect [see Goldblatt and Watson, 2012, for a recent review]. If the solar luminosity were beyond a certain threshold, the increased evaporation of water would result in accelerating warming. Eventually, all ocean water would be evaporated and lost to space by photodissociation and hydrodynamic escape, a process which is believed to be responsible for the lack of water in the atmosphere of Venus [Ingersoll, 1969; Rasool and de Bergh, 1970].

It has been estimated that a 10% increase in solar flux could have led to rapid loss of water from the early Earth [Kasting, 1988]. Taking into account the mass-luminosity relation in equation (4), the change in Earth's semi-major axis due to solar mass change from equation (5) and the secular evolution of solar luminosity following equation (1), this corresponds to a 7% increase in solar mass



[Whitmire *et al.*, 1995], so high mass loss could make the Archean unsuitable for life.

Furthermore, it has been suggested [Guzik and Cox, 1995] that an extended mass loss of the early Sun can be ruled out using helioseismology, the study of the Sun’s interior structure using resonant oscillations [Deubner and Gough, 1984]. Solving the faint young Sun problem would require that the Sun remained at least a few percent more massive than today over one or two billion years, while helioseismology limits the enhanced mass loss to the first 0.2 Gyr of the Sun’s life [Guzik and Cox, 1995]. A more extended period of mass loss leads to changes in the distribution of heavier elements below the solar convection zone, resulting in differences between calculated and observed oscillation frequencies. Guzik and Cox’s model of the interior of the Sun has been criticized by Sackmann and Boothroyd [2003], however, who claim that models with initial masses up to 7% higher than today are compatible with helioseismological observations.

Much more stringent limits to a more massive young Sun can be inferred from observations of mass loss in young stars similar to the Sun [Wood, 2004; Wood *et al.*, 2005]. Observations of other cool stars show that they lose most of their mass during the first 0.1 Gyr [Minton and Malhotra, 2007]. Most importantly, the observed solar analogs exhibit considerably lower cumulative mass-loss rates than required to offset the low luminosity of the early Sun [Minton and Malhotra, 2007]. The solution to the faint young Sun problem therefore seems to lie in the other parameters controlling Earth’s surface temperature, for example the concentration of greenhouse gases in the early atmosphere, rather than in a modification of the standard solar model involving higher mass-loss rates.

## 5. ENHANCED GREENHOUSE EFFECT

In today’s climate, the temperature of Earth’s troposphere is increased due to the absorption of long-wave radiation from the surface by atmospheric gases like water vapor, carbon dioxide, and methane. This greenhouse effect [Mitchell, 1989] has a natural and an anthropogenic component. The natural greenhouse effect is the cause for global average temperatures above the freezing point of water over much of the Earth’s history, while the anthropogenic component resulting from the continuing emission of greenhouse gases by humanity is responsible for the observed global warming since the 19th century [Solomon *et al.*, 2007].

Therefore, one obvious possibility to explain a warm early atmosphere despite a lower insolation

is an enhanced warming effect due to atmospheric greenhouse gases like ammonia ( $\text{NH}_3$ ), methane ( $\text{CH}_4$ ), or carbon dioxide ( $\text{CO}_2$ ).

### 5.1. Ammonia

Ammonia is a very powerful natural greenhouse gas [Wang *et al.*, 1976] because it has a strong and broad absorption feature at  $\sim 10 \mu\text{m}$  coincident with the peak in black-body emission from Earth’s surface. Ammonia seemed an attractive solution to the faint young Sun problem in early studies for a number of historic reasons. Indeed, in their original paper on the faint young Sun problem, Sagan and Mullen [1972] suggest that an ammonia greenhouse could have compensated the lower solar irradiance to keep Earth’s oceans from freezing over.

Historically, the choice of greenhouse gases like  $\text{NH}_3$  (and  $\text{CH}_4$  discussed in Section 5.2) as greenhouse gases was motivated by three arguments: the assumption that the early atmosphere was reducing, the apparent requirement of a reducing atmosphere for the production of organic molecules, and the widespread glaciations at the beginning of the Proterozoic. These historic arguments will be explored in the following.

The view held at that time that Earth’s early atmosphere was reducing is closely linked to theories of planetary formation. Earth was formed by accretion of smaller bodies (planetesimals) formed in the solar nebula [Wetherill, 1990] and may have formed a primary atmosphere from gases (predominantly hydrogen) present in the nebula. This primary atmosphere (if present) was quickly lost, however, and the secondary atmosphere was generated by outgassing of volatiles originally contained as chemical compounds within the planetesimals [Kasting, 1993]. A few decades ago, the accretion was believed to have been slow, leading to a late formation of Earth’s iron core. The iron would thus have remained in the mantle for some time and favored the formation of reducing gases that could then have accumulated in the early atmosphere.

It is now believed, however, that the early atmosphere was not strongly reducing. It was already pointed out in the 1960s and 1970s that geochemical evidence for such an atmosphere is lacking [Abelson, 1966] and that a strongly reducing atmosphere of the early Earth is unlikely, since the geochemistry of the upper mantle and the crust suggest that the material was not in contact with metallic iron [Walker, 1976]. This implies a rapid formation of Earth’s iron core and an oxidation state of the mantle and the atmosphere not too different from today. An additional argument in favor of a fast accretion of Earth is the early formation of the Moon  $\sim 4.5 \text{ Ga}$  [Canup, 2004]. The prevailing theory for the formation of the Moon suggests that the Moon was created when a large

(roughly Mars-sized) impactor hit the young Earth [Hartmann and Davis, 1975; Cameron and Ward, 1976; Canup, 2004], requiring the accumulation of a significant amount of material before the impact.

The second historically common argument in favor of a reducing early atmosphere is that reducing gases appeared to be required for the formation of the building blocks of life through lightning [Orgel, 1998; Chyba, 2010]. The famous experimental demonstration that electric discharges in a strongly reducing gas mixture containing methane, ammonia and hydrogen (then believed to resemble the early atmosphere) produce a variety of simple organic molecules [Miller, 1953; Miller and Urey, 1959] led many to believe in this scenario for the origin of prebiotic molecules. Indeed, in early papers on the faint young Sun problem Sagan and Mullen [1972] remark that ammonia is “a very useful precursor compound for prebiological organic chemistry” and Sagan [1977] states that “reduced atmospheric components such as  $\text{NH}_3$  and  $\text{CH}_4$  are required to understand the accumulation of prebiological organic compounds necessary for the origin of life”.

There are other scenarios for the production of prebiotic molecules which present viable alternatives to the Miller–Urey pathways, however. One possibility is that organic molecules were delivered by meteorites (in particular carbonaceous chondrites) or synthesized during impacts [Chyba and Sagan, 1992]. Another scenario for the production of biological precursor molecules relies on prebiotic chemistry taking place in deep-sea hydrothermal vents, arguably the most likely location for the origin of life anyway [Martin et al., 2008]. Finally it should be noted that substantial amounts of organic compounds like formaldehyde ( $\text{CH}_2\text{O}$ ) [Pinto et al., 1980] and hydrogen cyanide ( $\text{HCN}$ ) [Abelson, 1966; Zahnle, 1986] are photocemically produced even in weakly reducing atmospheres, where the latter requires the presence of methane. It should be noted that a very low atmospheric ammonia concentration of  $\sim 10^{-8}$  required for the evolution of life [Bada and Miller, 1968] can also be maintained in an atmosphere with high concentrations in carbon dioxide [Wigley and Brimblecombe, 1981].

The third frequently used argument in favor of reducing greenhouse gases like  $\text{NH}_3$  and  $\text{CH}_4$  is that the major “Huronian” glaciations of the planet occurring in the time interval 2.4 – 2.2 Ga could have been triggered by the first major rise of atmospheric oxygen [see Canfield, 2005; Catling and Claire, 2005; Holland, 2006; Sessions et al., 2009, for recent reviews] around the same time. The increase in atmospheric  $\text{O}_2$  would have dramatically diminished the concentration of  $\text{CH}_4$  and other reducing greenhouse gases like  $\text{NH}_3$  via oxi-

dation, resulting in global cooling [Kasting et al., 1983; Pavlov et al., 2000; Kasting et al., 2001; Kasting, 2005; Kopp et al., 2005; Haqq-Misra et al., 2008]. The relative timing of these events is obviously crucial, and it now appears that the first global glaciation occurred close to 2.4 Ga [Kirschvink et al., 2000] and thus before the Great Oxidation Event which is dated closer to 2.3 Ga and thus around the time of the second of three Huronian glaciations [Bekker et al., 2004]. Furthermore, there is evidence for an even earlier continental glaciation from glacial deposits in the Pongola Supergroup dated  $\sim 2.9$  Ga [Young et al., 1998] although it remains unclear whether this was a global event. Distinct pulses of oxygenation associated with those glaciations might explain these findings; in any case, the argument is not as clear-cut as often suggested.

Thus most of these historic arguments in favor of ammonia (and other reducing greenhouse gases) have now been put into perspective, but it remains interesting to see how much ammonia would be required to offset the faint young Sun. In their paper, Sagan and Mullen [1972] used a simple two-layer approximation to the atmosphere’s energy budget to show that early Earth could have been kept warm by very low partial pressures ( $p_{\text{NH}_3} = 10^{-5}$  bar) of ammonia added to an atmosphere with a total pressure of 1 bar and today’s concentrations of carbon dioxide and water vapor ( $\text{H}_2\text{O}$ ) as well as volume mixing ratios of  $10^{-5}$  of methane and hydrogen sulfide ( $\text{H}_2\text{S}$ ), see Figure 3. For comparison, the partial pressure of ammonia in the present-day atmosphere is only  $6 \times 10^{-9}$  bar [Wang et al., 1976]. The Archean Earth surface temperatures of  $T_s \simeq 340$  K derived in Sagan and Mullen [1972] for their ammonia-dominated greenhouse are actually considerably above the normal freezing point of water.

Despite its strong warming effect, subsequent studies of the faint young Sun problem revealed difficulties with ammonia as the dominant greenhouse gas in the Archean. Kuhn and Atreya [1979] used a more sophisticated radiative transfer model and confirmed the results of Sagan and Mullen [1972] by showing that  $\text{NH}_3$  partial pressures larger than  $p_{\text{NH}_3} = 8 \times 10^{-6}$  bar for an albedo of 0.30 and an atmosphere with a total pressure of 0.78 bar, present-day water vapor content and a carbon dioxide partial pressure of  $p_{\text{CO}_2} = 3.6 \times 10^{-4}$  bar are sufficient to keep Earth from freezing. They pointed out one significant problem, however, which had earlier been noted by Abelson [1966]: using models for the photochemistry of ammonia, they demonstrated that the Sun’s ultraviolet radiation (which was much more intense during the Archean, see Section 2.1) would have destroyed this amount of  $\text{NH}_3$  via photodissociation in less than a decade.

They conclude that continuous outgassing of ammonia from the Earth’s interior would have been required to make an  $\text{NH}_3$  greenhouse during the Archean work.

Investigating this balance between outgassing and photochemical destruction, *Kasting* [1982] estimated steady-state ammonia formation rates for the early Earth and concluded that abiotic sources could have been sufficient to sustain mixing ratios of  $\sim 10^{-8}$  which have been argued to be required for the evolution of life in the ocean based on the rapid decomposition of aspartic acid in the absence of ammonium and the assumption that aspartic acid is necessary for life to originate [*Bada and Miller*, 1968]. The ammonium resupply rates derived in *Kasting* [1982] are insufficient to provide substantial greenhouse warming, however.

It should also be noted that ammonia is highly soluble [*Levine et al.*, 1980] and thus quickly rained out of the atmosphere and dissolved as ammonium ( $\text{NH}_4^+$ ) in the oceans [*Kasting*, 1982; *Walker*, 1982]. Sustaining atmospheric partial pressures of ammonia in the range required to offset the faint young Sun requires 0.1–10 percent of the atmospheric nitrogen to be dissolved in the ocean [C. Goldblatt, private communication].

Due to these problems, ammonia had fallen out of favor as the dominant greenhouse gas in the Archean atmosphere. More recently, *Sagan and Chyba* [1997] revived the idea of an Archean ammonia greenhouse by pointing out that an early atmosphere containing nitrogen ( $\text{N}_2$ ) and  $\text{CH}_4$  would form an organic haze layer produced by photolysis. This layer would block ultraviolet radiation and thus protect  $\text{NH}_3$  from photodissociation. Others showed, however, that the existence of such a layer would lead to an ‘anti-greenhouse’ effect because it blocks solar radiation from reaching the surface but allows thermal radiation to escape to space [*McKay et al.*, 1991, 1999]. High humidity has been shown in experimental studies to further enhance this cooling effect of aerosols [*Hasenkopf et al.*, 2011]. Furthermore, the size distribution of the haze particles could have limited the layer’s shielding function against solar ultraviolet radiation [*Pavlov et al.*, 2001], although laboratory experiments suggest particle sizes which make the haze optically thick in the ultraviolet yet optically thin in the optical [*Trainer et al.*, 2006].

The ammonia story took an unexpected turn recently, when *Ueno et al.* [2009] suggested that carbonyl sulfide (OCS) at ppmv (parts per million volume) levels could explain the distribution of sulfur isotopes in geological samples from the Archean and could shield  $\text{NH}_3$  against ultraviolet radiation. Detailed photochemical modeling shows, however, that such high concentrations of OCS are unlikely because OCS is rapidly photodissociated in the ab-

sence of ultraviolet shielding by ozone [*Domagal-Goldman et al.*, 2011].

As an additional argument against the cooling effects of haze layers, *Wolf and Toon* [2010] demonstrated in a general circulation model with size-resolved aerosols that the fractal structure of the aerosol particles forming the haze drastically diminishes the anti-greenhouse effect. Such fractal particles give a good fit to the albedo spectrum of Titan, the largest moon of Saturn, which has a dense atmosphere with an opaque organic haze layer [*Danielson et al.*, 1973; *Rages and Pollack*, 1980, 1983; *McKay et al.*, 1991]. In addition, *Hasenkopf et al.* [2011] showed that the aerosol particles in the haze could have led to the formation of short-lived and optically thin clouds with a lower albedo than today’s clouds, hence decreasing their cooling and increasing their warming effect. (Note, however, that cloud effects alone are insufficient to effectively counteract the faint young Sun, see Section 6.)

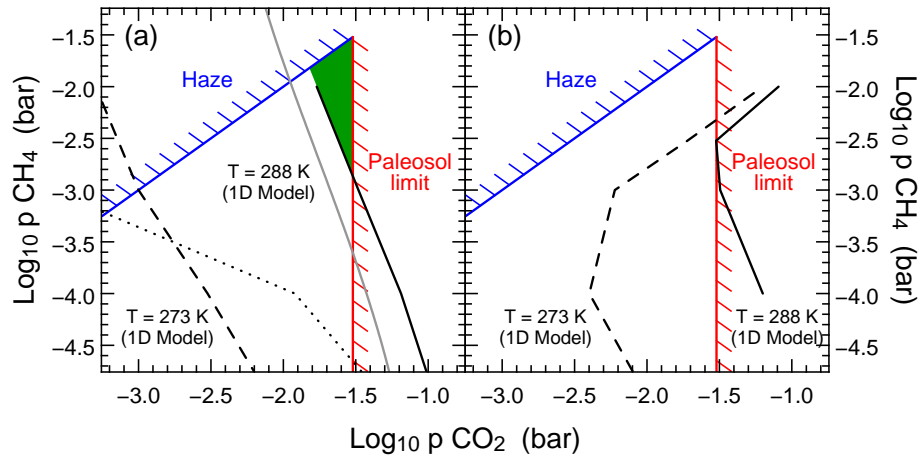
In summary, ammonia may not be completely out of the game as a possible solution of the faint young Sun problem after all, although potential problems with the haze shielding and the high solubility of ammonia appear to make  $\text{CH}_4$  and  $\text{CO}_2$  more likely candidates.

## 5.2. Methane

Given the problems with ammonia as a greenhouse gas in the Archean, some researchers turned to methane ( $\text{CH}_4$ ) as a potential warming agent for the Archean climate.

The main advantage of methane as compared to ammonia discussed in Section 5.1 above is that  $\text{CH}_4$  is photolyzed considerably slower than  $\text{NH}_3$ , because it requires ultraviolet light of much shorter wavelengths ( $\lesssim 145$  nm) where the Sun emits less radiation. Indeed, photochemical models show that even under the more intense ultraviolet radiation emitted by the young Sun, the lifetime of  $\text{CH}_4$  in a terrestrial atmosphere low in  $\text{CO}_2$  is of the order of  $10^3$  to  $10^4$  years [*Zahnle*, 1986], in contrast to less than 10 years for  $\text{NH}_3$ .

There are two effects constraining the allowed parameter space for a methane greenhouse on the early Earth, though. First, depending on the assumed atmospheric methane partial pressure, a contribution from other greenhouse gases to the warming will be required, with carbon dioxide being the most natural choice. As discussed in Section 5.3 below, geochemical data from ancient paleosols set an upper limit to the atmospheric carbon dioxide partial pressure of at most  $p_{\text{CO}_2} < 0.03$  bar during the late Archean. Scenarios with low methane partial pressures could be in conflict with this constraint, unless other forcings contribute to warming.



**Figure 4.** Parameter space for a late-Archean methane greenhouse. (a) The solid black line shows the methane and carbon dioxide partial pressures required to sustain a global average surface temperature  $T = 288$  K based on the model calculations for a  $\text{CH}_4$ - $\text{CO}_2$ - $\text{H}_2\text{O}$  greenhouse at 1 bar total pressure and a solar luminosity of  $0.8 L_\odot$  corresponding to a time 2.8 Ga [Haqq-Misra et al., 2008]; the dashed line indicates the partial pressures for  $T = 273$  K. Earlier model calculations for  $T = 288$  K are also shown: the results from Kiehl and Dickinson [1987] as gray line and the erroneous results from Pavlov et al. [2000] as dotted line. The limit of haze formation is indicated in blue, the paleosol upper limit on the  $\text{CO}_2$  partial pressure in red. The small green triangle shows the possible parameter space for greenhouse warming sufficient to prevent global glaciation given the constraints from haze formation and paleosol geochemistry. (b) Same as (a), but for model calculations explicitly taking into account additional warming by ethane ( $\text{C}_2\text{H}_6$ ) and cooling by organic haze [Haqq-Misra et al., 2008]. A total atmospheric pressure  $p = 1$  bar is assumed when converting from volume mixing ratios to partial pressures.

Secondly, photochemical models show that an organic haze starts to form at high  $\text{CH}_4/\text{CO}_2$  ratios [Kasting et al., 1983]. As discussed above, an organic haze layer exhibits an anti-greenhouse effect because it reflects solar radiation back into space while being transparent to outgoing infrared radiation [McKay et al., 1991, 1999]. This haze would thus cool the planet, effectively limiting the greenhouse warming achievable by methane in the early atmosphere. Earlier photochemical modeling indicated that organic haze should form in the primitive atmosphere at  $\text{CH}_4/\text{CO}_2$  ratios larger than 1 [Zahnle, 1986; Pavlov et al., 2001]. Recent laboratory experiments [Trainer et al., 2004, 2006] suggest that haze could start to form at even lower mixing ratios of  $\sim 0.2 - 0.3$ . Note, however, that the fractal nature of haze particles already discussed in the context of a possible shielding of ammonia from ultraviolet radiation would have limited the anti-greenhouse effect of the haze layer [Wolf and Toon, 2010].

Moreover, laboratory experiments show that enhanced concentrations of up to 15% of hydrogen ( $\text{H}_2$ ) decrease the amount of haze formed in a  $\text{CO}_2$ -rich atmosphere and thus limit the anti-greenhouse effect while providing sufficient warming for the Archean Earth [DeWitt et al., 2009]. The amount of hydrogen in the early atmosphere is determined by the balance between volcanic outgassing and hydrogen escape to space. Conventional wisdom suggests that hydrogen escape on early Earth is lim-

ited by upward diffusion [Hunten, 1973; Walker, 1977], resulting in atmospheric hydrogen mixing ratios of the order of  $10^{-3}$ . It has been argued, however, that in the anoxic early atmosphere temperatures at the base of exosphere (the outermost atmospheric layer) would have been much lower, resulting in considerably slower hydrogen escape and thus larger hydrogen mixing ratios [Watson et al., 1981; Tian et al., 2005]. Tian et al. [2005] estimated molecular hydrogen mixing ratios of up to 30% in the early atmosphere. This notion of a hydrogen-rich early atmosphere remains controversial, however [Catling, 2006; Tian et al., 2006] and should be investigated with photochemistry models which are more appropriate than the models used so far. It is also unclear whether such a large hydrogen inventory would be maintained in the presence of methanogenic bacteria which consume hydrogen in their metabolism.

But how much methane would be required to warm the Archean atmosphere, and how does this compare to the constraints from paleosols and haze formation? Kiehl and Dickinson [1987] were the first to calculate the potential contribution of methane to an Archean  $\text{CO}_2$  greenhouse (see Figure 4a). According to their calculations,  $\text{CO}_2$  partial pressures of  $p_{\text{CO}_2} \sim 0.1$  bar and  $p_{\text{CO}_2} \sim 0.03$  bar would be sufficient to reach average surface temperatures similar to today for the early and late Archean, respectively, when methane at a mixing ratio of  $10^{-4}$  is present in the atmosphere. These values for the carbon dioxide partial pres-

sure are about a factor of  $\sim 3$  lower than without methane, see the discussion in Section 5.3.

Quite a bit of confusion has been caused by the subsequent study by *Pavlov et al.* [2000] which reported considerably stronger warming in a late-Archean methane greenhouse as compared to *Kiehl and Dickinson* [1987], in particular at higher methane partial pressures (see Figure 4a). Unfortunately, these results were due to an error in the radiative-transfer code, and revised calculations [*Haqq-Misra et al.*, 2008] show a methane warming that is actually smaller (at a given methane concentration) than the earlier calculations by *Kiehl and Dickinson* [1987]. These model calculations are compared to the constraints from haze formation and geochemistry of paleosols in Figure 4a, leaving only a small triangle in the  $\log p_{\text{CH}_4} - \log p_{\text{CO}_2}$  parameter space where sufficient warming can be provided without cooling by organic haze and without conflict with the paleosol constraints on  $p_{\text{CO}_2}$ . Note that, depending on temperature, the upper limits on carbon dioxide partial pressure could be even lower (see Figure 6 and the discussion below). It is less clear how tight the constraint from haze formation is in reality as, on the one hand, haze could be formed at even lower  $\text{CH}_4/\text{CO}_2$  mixing ratios [*Trainer et al.*, 2004, 2006], but could exhibit a decreased anti-greenhouse effect due to the fractal nature of the aerosol particles forming the haze layer [*Wolf and Toon*, 2010], see the discussion in Section 5.1 above.

The recent model calculations by *Haqq-Misra et al.* [2008] taking into account the anti-greenhouse effect of (non-fractal) organic haze (which starts to form at  $\text{CH}_4/\text{CO}_2$  mixing ratios of  $\sim 0.1$  in their model, in agreement with the laboratory results discussed above) and additional warming by ethane ( $\text{C}_2\text{H}_6$ ) are shown in Figure 4b. According to these simulations, a late-Archean  $\text{CO}_2\text{-CH}_4$  solution to the faint young Sun problem appears to be more complicated than previously thought because organic haze formation sets in at higher methane partial pressures while high carbon dioxide partial pressures are ruled out by paleosol constraints, yielding insufficient warming to explain the absence of glaciation in the late Archean. This strongly depends on the still somewhat obscure properties of organic haze layers in the early atmosphere, however, and other gases besides  $\text{CO}_2$  and  $\text{CH}_4$  might have contributed to the warming.

Finally, although methane is considerably more stable than ammonia, it is continuously depleted by photolysis and reactions with hydroxyl (OH) radicals. Thus it is interesting to ask what con-

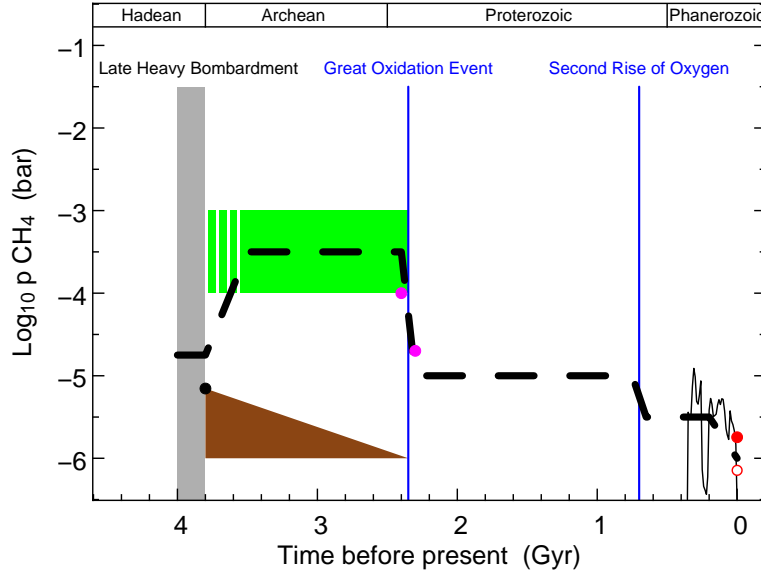
straints on Archean methane fluxes and atmospheric concentrations can be derived.

Before discussing estimates of atmospheric methane concentrations during the Archean, we take a brief look at the methane budget of today's atmosphere. The methane concentration in the present-day atmosphere is about 1.8 ppmv, having increased from  $\sim 0.7$  ppmv in pre-industrial times due to anthropogenic methane emissions from agriculture and industrial processes [*Forster et al.*, 2007]. Methane sources today amount to a methane flux of about  $600 \text{ Tg yr}^{-1}$  ( $1 \text{ Tg} = 10^{12} \text{ g}$ ) [*Denman et al.*, 2007]. In the literature, estimates for Archean methane fluxes are often compared to this present-day flux (frequently and inaccurately even called the “current biological flux”). This is of course a valid order-of-magnitude comparison in principle, but it should be kept in mind that more than 60% of today's methane flux is from anthropogenic sources (including industrial processes and emissions related to fossil fuels), and about 90% of the remaining natural flux originates from ecosystems which were not present during the Archean, i.e., wetlands, termites, wild animals and wildfires [*Denman et al.*, 2007].

Today, methane is predominantly produced biologically. In the Archean, three sources of methane have contributed to the atmospheric budget: impacts from space, geological sources, and anaerobic ecosystems [*Kasting*, 2005], see Figure 5 for an overview.

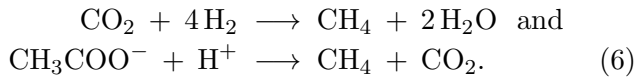
Very high methane fluxes from cometary impacts of  $\gtrsim 500 \text{ Tg yr}^{-1}$  at 3.5 Ga and  $\gtrsim 5000 \text{ Tg yr}^{-1}$  at 3.8 Ga have been estimated by *Kress and McKay* [2004] based on impact rates derived in *Chyba* [1990]. More modest  $\text{CH}_4$  production rates appear more likely, however. *Kasting* [2005] estimates an methane flux from impacts at the beginning of the Archean 3.8 Ga of  $\sim 20 \text{ Tg yr}^{-1}$ . Using the non-linear relation between methane source flux and atmospheric concentration based on photochemical modeling given in *Kasting* [2005] and based on [*Pavlov et al.*, 2001], this corresponds to a volume mixing ratio  $\sim 7$  ppmv.

The order of magnitude of geological methane sources in the Archean can be derived from the present-day abiogenic methane flux. The current flux from mineral alteration at mid-ocean ridges, emissions from volcanoes, and geothermal sources based on the most recent data has been estimated to be  $\sim 2.3 \text{ Tg yr}^{-1}$  [*Emmanuel and Ague*, 2007], sufficient to sustain  $\sim 1$  ppmv according to *Kasting* [2005]. In the early Archean, this flux could have been a factor of 5 to 10 larger due to the faster creation of seafloor on early Earth [*Kasting*, 2005], resulting in an atmospheric mixing ratio of  $\sim 7$  ppmv.



**Figure 5.** Estimates for the methane partial pressure in the atmosphere in various epochs in Earth’s history. The period of frequent impacts during the Late Heavy Bombardment is shown in *gray*, with the estimate for methane produced in impacts by *Kasting [2005]* as *black circle*. The *green area* indicates the range based on estimates of biological methane fluxes during the Archean [*Kasting, 2005*]. The *brown triangle* shows the contribution from abiogenic sources based on the present-day estimate of *Emmanuel and Aque [2007]*, including a possible increase up to a factor of 10 in earlier times due to faster creation of seafloor [*Kharecha et al., 2005*]. The decrease with time is not based on any detailed model but only intended to give a rough indication of this possibility. Estimates for atmospheric methane content from a model of the Great Oxidation Event are indicated in *magenta* [*Goldblatt et al., 2006*]. Phanerozoic  $\text{CH}_4$  concentrations estimated in *Beerling et al. [2009]* are represented by the *thin black line*. Finally, the pre-industrial and present-day methane partial pressures are shown as *open* and *filled red circle*, respectively [*Forster et al., 2007*]. The *thick black dashed line* is a highly idealized sketch of Earth’s methane history based on these estimates. Methane fluxes have been converted to atmospheric mixing ratios using the relation shown in *Kasting [2005]*, and a total pressure  $p = 1$  bar is assumed for the conversion from volume mixing ratios to partial pressure values.

Therefore, low concentrations of the order of 10 ppmv of methane in the atmosphere could have been sustained from abiogenic sources in the early Archean. Later in time, after the origin of life and before the first major rise in atmospheric oxygen, much larger methane concentrations can be achieved from biological sources. Biological methane production today is accomplished by methanogenic bacteria (or methanogens for short) which are believed to have arisen very early in the evolution of life [*Woese and Fox, 1977*]. Their metabolism is based on a variety of metabolic pathways [*Thauer, 1998*]. The two most important net reactions are



Assuming that methanogens converted most of the hydrogen available in the atmosphere [*Kral et al., 1998; Kasting et al., 2001*] and using an estimated hydrogen mixing ratio of  $(1 - 2) \times 10^{-3}$ , Archean methane mixing ratios of 500–1000 ppmv could be plausible. More elaborate simulations with a coupled photochemistry-ecosystem model

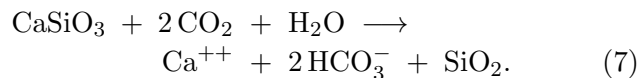
essentially confirm these early estimates, with atmospheric methane mixing ratios in the range 100–1000 ppmv for reasonable atmospheric hydrogen fractions [*Kharecha et al., 2005*]. It should be noted that our understanding of Archean ecosystems is naturally rather limited, so these estimates should be taken with a grain of salt.

Nevertheless, from these arguments one can conclude that methane mixing ratios in the Archean atmosphere of up to 1000 ppmv appear plausible, see Figure 5. Comparing this to the results from climate model simulations for the late-Archean presented in Figure 4, it is obvious that these are insufficient to provide enough warming given the paleosol constraints on carbon dioxide partial pressures during that time. Even if higher methane fluxes should have been achieved, haze formation limits the warming in a late-Archean methane greenhouse, although this depends on the details of organic-haze formation and the properties of the particles within the haze layer, see the discussion above. Note that the production of haze is self-limiting, as more haze would cool the climate and thus reduce the amount of methane produced by methanogens [*Domagal-Goldman et al., 2008*].

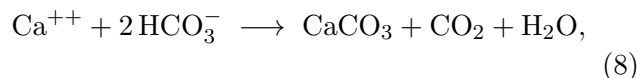
In summary, it remains unclear whether methane could have provided sufficient warming at least for the late Archean, but a solution of the faint young Sun problem based on methane certainly appears to be considerably more complicated than previously thought.

### 5.3. Carbon Dioxide

Due to the increasing amounts of arguments against a strongly reducing early atmosphere [Walker, 1976], carbon dioxide was suggested early on as the dominant greenhouse gas counteracting the faint young Sun on Earth [Owen *et al.*, 1979; Walker *et al.*, 1981; Kuhn and Kasting, 1983; Kasting *et al.*, 1984; Kasting and Ackerman, 1986; Kasting, 1987] and Mars [Cess *et al.*, 1980]. Carbon dioxide is an attractive solution to the faint young Sun problem in the sense that the long-term evolution of the atmospheric carbon dioxide concentration is controlled by the inorganic carbon cycle, part of an important negative feedback loop which stabilizes Earth's climate on geological timescales [Walker *et al.*, 1981; Berner *et al.*, 1983]. The inorganic carbon cycle removes CO<sub>2</sub> from the atmosphere via silicate weathering according to the reaction



(For illustrative purposes the silicate mineral wollastonite, CaSiO<sub>3</sub>, is taken here to represent all silicate rock.) The products of this reaction are transported by rivers to the oceans, where they are – biotically or abiotically – converted into calcium carbonate:



resulting in the net formula for the so-called Urey silicate-weathering reaction



This precipitated calcium carbonate is then partly deposited in sediments at the bottom of the oceans. The sediments on the seafloor are then transported via the motions of plate tectonics. At subduction zones, most of the carbon dioxide is returned to the atmosphere via arc volcanism, while some is incorporated into the Earth's mantle, depending on the composition of the sediments and temperature [Kerrick and Connolly, 2001; Stern, 2002]. Quite remarkably, the basic principles of the inorganic carbon cycle were already discovered by

several scientists in the 19th century [see Berner, 1995; Berner and Maasch, 1996, for discussions of this early history of ideas about the inorganic carbon cycle].

The silicate-weathering cycle is part of a negative feedback loop because the weathering rate removing CO<sub>2</sub> from the atmosphere increases with growing atmospheric CO<sub>2</sub> concentrations and rising temperatures (and vice versa), while the volcanic emission of CO<sub>2</sub> can be assumed to be roughly constant over geological time (when averaged over sufficiently long timescales to suppress the large variations caused by individual eruptions), or possibly decreasing over time governed by changes in geothermal heat flow and volcanic activity.

Following the initial work on carbon dioxide in the Archean atmosphere, one-dimensional radiative-convective climate models were used to estimate the amount of CO<sub>2</sub> necessary to keep Earth from freezing (see also Figure 6). For solar luminosities of  $L = 0.75 L_\odot$  representative for the early Archean, these models suggest that carbon dioxide partial pressures of  $p_{\text{CO}_2} \simeq 0.3$  bar (or more than 1,000 times the pre-industrial value of  $p_{\text{CO}_2} \simeq 0.00028$  bar) are required to reach global average surface temperatures similar to today, i.e.,  $T_s \simeq 288$  K, whereas partial pressures of  $p_{\text{CO}_2} \simeq 0.1$  bar (about 300 times the present-day value) are sufficient for the late Archean [Owen *et al.*, 1979; Kasting *et al.*, 1984; Kiehl and Dickinson, 1987; von Paris *et al.*, 2008].

A temperature of 288 K would presumably correspond to a world with small ice caps similar to our present climate, the limit of complete freezing is often set at a mean surface temperature of 273 K, the freezing point of water. Carbon dioxide values required to reach this temperature are typically  $p_{\text{CO}_2} \simeq 0.06$  bar (or about 200 times pre-industrial levels) for the early Archean and  $p_{\text{CO}_2} \simeq 0.01$  bar (roughly 30 times pre-industrial levels) for the late Archean, respectively. These numbers are generally interpreted as lower limits, since the ice-albedo feedback (and many other factors) are not adequately considered in these calculations, but note that some studies [e.g., Kasting, 1987, 1993] crudely account for the ice-albedo feedback effect by requiring a minimum mean surface temperature of 278 K based on recent glaciations, thus yielding higher CO<sub>2</sub> concentrations than the ones reported for 273 K mean surface temperature reported above (0.1 bar and 0.03 bar CO<sub>2</sub> partial pressure for the beginning and end of the Archean, respectively).

Note that the inorganic carbon cycle operates on very long timescales, so the question arises of whether such high carbon dioxide concentrations are sufficient to *stabilize* the climate in the



Archean. The timescales for increasing the atmospheric  $\text{CO}_2$  concentration due to faster rates of volcanic outgassing and/or slower rates of weathering ( $\sim 10^5$  yr) are much longer than the ones for the formation of snow and ice ( $\sim 1$  yr), so any transient cooling would lead to global glaciation [Caldeira and Kasting, 1992]. It has been furthermore suggested that the formation of highly reflective  $\text{CO}_2$  clouds in the atmosphere could make this glaciation irreversible. Carbon dioxide ice clouds scatter solar radiation and thus raise the albedo, but were assumed to be nearly transparent to thermal radiation. They were therefore expected to cool the planet [Kasting, 1991]. This would be true if the clouds were composed of particles smaller than a few micrometers in size, but larger particles can be expected in such clouds which then would scatter infrared radiation very effectively and thus result in a net warming effect [Forget and Pierrehumbert, 1997], provided that they are not low and optically thick [Mischna *et al.*, 2000].

Carbon dioxide as the dominant greenhouse gas offsetting the faint early Sun has been criticized on two grounds, however. First, it has been argued that the removal of atmospheric carbon dioxide during the Archean was dominated by the flow of carbon into the mantle via the subduction of carbonatized seafloor on a tectonically more active Earth rather than silicate weathering [Sleep and Zahnle, 2001]. This would constantly diminish the atmospheric reservoir of  $\text{CO}_2$ , thus decreasing its warming effect on the Archean climate. This may not be a major problem for the notion of carbon dioxide as main warming agent during the Archean, however, since at low  $\text{CO}_2$  levels (and in the absence of other greenhouse gases) the flow of carbon dioxide from the atmosphere to the ocean is limited by the ice cover on the oceans.

Secondly, and most importantly, geochemical analysis of paleosols and banded iron formations provides constraints on the atmospheric  $\text{CO}_2$  concentration during the late Archean to values much lower than required to solve the faint young Sun problem, see Figure 6. Rye *et al.* [1995] used the absence of siderite ( $\text{FeCO}_3$ ) and a thermodynamic model for the mineral assemblage in 2.2–2.75 Gyr-old paleosols to establish an upper limit of about 100 times present-day levels. During anoxic weathering of basalt, iron is washed out of the upper layers of soils and either transferred to the ground water or precipitated within the mineral assemblage. At high  $\text{CO}_2$  partial pressures, siderite would be expected to be found in the lower parts, at low  $\text{CO}_2$  levels the iron would be precipitated in the form of iron silicates. Siderite is absent from all of the paleosols older than 2.2 Gyr, however, whereas

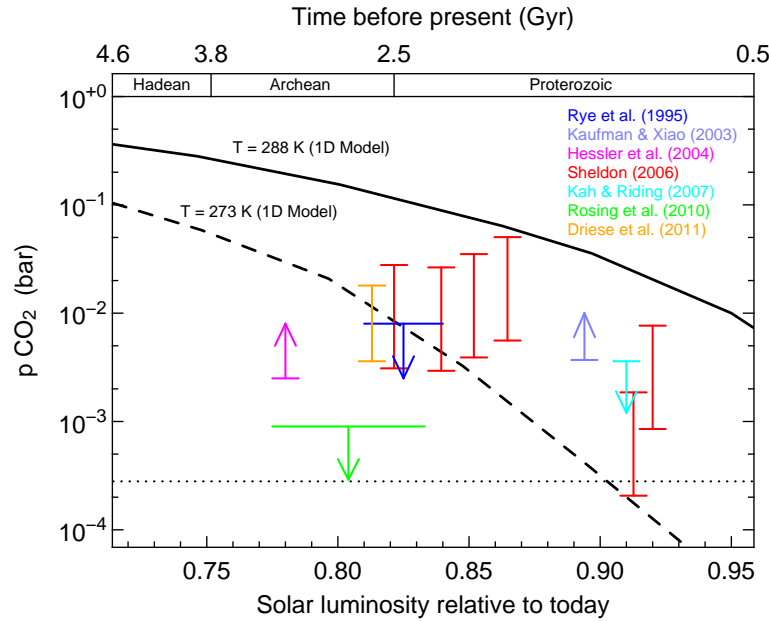
other iron-rich minerals are found, suggesting low atmospheric  $\text{CO}_2$  levels during the late Archean and early Proterozoic.

Conflicting evidence for a  $\text{CO}_2$ -rich atmosphere during the Archean and early Proterozoic based on the occurrence of siderite in banded iron formations [Ohmoto *et al.*, 2004; Ohmoto and Watanabe, 2004] was convincingly challenged [Kasting, 2004; Sleep, 2004; Sheldon, 2006].

Even lower values for the  $\text{CO}_2$  levels in the early Proterozoic were later derived by Sheldon [2006] from an improved model relying on the mass balance of weathering rather than the thermodynamic argument used in Rye *et al.* [1995], yielding a range of  $p_{\text{CO}_2} \sim 0.003 - 0.03$  bar for three samples of  $\sim 2.2$  Gyr-old paleosols, and values in a similar range for samples with ages from 2.5 to 1.8 Gyr. Applying the same method to a late-Archean paleoweathering profile dated at 2.69 Ga yields a range of  $\text{CO}_2$  partial pressures  $p_{\text{CO}_2} \sim 0.004 - 0.02$  bar [Driese *et al.*, 2011], consistent with the results obtained by Rye *et al.* [1995] and Sheldon [2006].

An even lower upper limit for the  $\text{CO}_2$  partial pressure in the Archean atmosphere was derived by Rosing *et al.* [2010]. In this paper, the authors argue that the coexistence of siderite and magnetite ( $\text{Fe}_3\text{O}_4$ ) in Archean banded iron formations constrain the atmospheric carbon dioxide concentration to only about 3 times the present-day level [see also Mel'nik, 1982; Kasting, 2010]. Note, however, that there is some controversy whether the formation of these minerals occurred in thermodynamic equilibrium with the atmosphere-ocean system [Dauphas and Kasting, 2011; Reinhard and Planavsky, 2011; Rosing *et al.*, 2011]. Indeed it is likely that a considerable fraction of these minerals were formed during diagenesis rather than in the supernatant water column and that the conversion of magnetite to siderite was limited by the rate of supply of organic matter rather than  $\text{CO}_2$ . The simultaneous occurrence of siderite and magnetite in banded iron formations might thus not provide any strong constraints on atmospheric  $\text{CO}_2$  partial pressure after all. The results published in Rosing *et al.* [2010] are also in conflict with lower limits derived from weathering rinds on 3.2-Gyr-old river gravels for which the presence of iron-rich carbonates requires  $\text{CO}_2$  partial pressures of about 10 times pre-industrial levels for the same environmental temperature of 298 K as in the Rosing *et al.* [2010] study [Hessler *et al.*, 2004].

Despite the uncertainties discussed above, geochemical data therefore suggest that  $\text{CO}_2$  partial pressures were likely smaller than a few hundred times pre-industrial levels in the late Archean and early Proterozoic, meaning that carbon dioxide alone would most likely have been unable to provide enough warming during these times (see again



**Figure 6.** Comparison of empirical estimates of carbon dioxide partial pressures during the Precambrian and climate model results for an average global surface temperature of 288 K assumed to be required to prevent global glaciation as a function of relative solar luminosity (*solid black line*). The results for a global mean temperature of 273 K are indicated by the *dashed black line*. Calculations are based on a one-dimensional radiative-convective climate model [von Paris et al., 2008]. Geochemical estimates for atmospheric CO<sub>2</sub> partial pressures at different epochs are indicated [Rye et al., 1995; Hessler et al., 2004; Sheldon, 2006; Rosing et al., 2010; Driese et al., 2011], see the text for details. A temperature of 298 K is assumed in case an explicit dependence of the estimates on environmental temperature is available. In addition to the Archean and Paleoproterozoic estimates, four Mesoproterozoic estimates are shown for comparison: a lower limit derived from a carbon isotope analysis of microfossils dating back 1.4 Ga [Kaufman and Xiao, 2003], a  $\sim 1.2$  Ga upper limit inferred from in-vivo experiments of cyanobacterial calcification [Kah and Riding, 2007] and two estimates from Sheldon [2006]. The dotted line shows the pre-industrial CO<sub>2</sub> partial pressure of  $2.8 \times 10^{-4}$  bar. The conversion from solar luminosity (bottom scale) to age (top scale) follows the approximation given in equation (1). Modified and updated after Kasting [2010].

Figure 6). In this context it should be kept in mind that all modeling studies which determine the CO<sub>2</sub> limit necessary to warm the early Earth rely on one-dimensional models with highly parametrized descriptions of many important feedback mechanisms like the ice-albedo feedback. A further complication arises from uncertainties in radiative transfer calculations for atmospheres rich in carbon dioxide [Halevy et al., 2009; Wordsworth et al., 2010]. The problem arises because the wings of absorption line profiles and the parameters governing the continuum absorption of CO<sub>2</sub> are poorly constrained by empirical data for the high CO<sub>2</sub> partial pressures used in calculations of the faint young Sun problem. Wordsworth et al. [2010], for example, suggest that the radiative transfer calculations used in many earlier studies overestimate the CO<sub>2</sub> absorption in the early atmosphere when compared to a parametrization which most accurately reflects presently available data.

It therefore remains to be seen whether carbon dioxide concentrations in agreement with geochem-

ical evidence are sufficient to offset the faint young Sun.

#### 5.4. Other greenhouse gases

Other greenhouse gases have been suggested to contribute to warming early Earth. For example, ethane (C<sub>2</sub>H<sub>6</sub>) is expected to form in an atmosphere containing methane and exposed to ultraviolet radiation [Haqq-Misra et al., 2008]. It has been shown that ethane can contribute to an Archean greenhouse [Haqq-Misra et al., 2008], although the effect is not large as can be seen in Figure 4. Warming by nitrous oxide (N<sub>2</sub>O) has been suggested [Buick, 2007], but N<sub>2</sub>O is rapidly photodissociated in the absence of atmospheric oxygen [Roberson et al., 2011], making it an unviable option for the Archean. Furthermore, carbonyl sulfide (OCS) at ppmv levels has the potential to offset the faint young Sun [Ueno et al., 2009], but it appears very unlikely that OCS concentrations higher than ppbv (parts per billion volume) level could have been maintained due to photodissociation losses [Domagal-Goldman et al., 2011].

Although nitrogen is not a greenhouse gas in itself, a higher partial pressure of atmospheric nitrogen during the Archean would amplify the greenhouse impact of other gases by broadening of absorption lines [Goldblatt *et al.*, 2009]. Despite the fact that this additional warming is partly compensated by increased Rayleigh scattering of short-wave radiation [Halevy *et al.*, 2009], model calculations show that it could cause a warming by 4.4°C for a doubling of the N<sub>2</sub> concentration [Goldblatt *et al.*, 2009]. Nitrogen outgassed quickly on early Earth, so the atmospheric nitrogen content likely equaled at least the present-day value. Since all nitrogen in the mantle today must have been processed through the atmosphere, the reservoirs in the crust and mantle appear sufficiently large to explain higher atmospheric concentrations and thus a warmer Archean [Goldblatt *et al.*, 2009].

### 5.5. Summary

In summary, an enhanced greenhouse effect arguably still seems the most likely solution to the faint young Sun problem. Carbon dioxide and methane are the most obvious candidates, although they could face severe difficulties in terms of geochemical constraints and low production rates, respectively, and their respective contribution remains uncertain. Ammonia appears less likely than CO<sub>2</sub> and CH<sub>4</sub> because it would have to be shielded against photodissociation by ultraviolet radiation and because it would be washed out by rain.

A final assessment of greenhouse-gas warming in the early atmosphere, however, is complicated by uncertainties in the radiative transfer functions and the lack of spatially-resolved and fully coupled climate models for the early Earth comprising the full range of feedbacks in the Earth system. Finally, other climatic factors like changes in cloud cover could in principle at least have contributed to a warming of the Archean Earth.

## 6. CLOUDS IN THE ARCHEAN ATMOSPHERE

Clouds exhibit two competing effects on the climate. On the one hand, clouds, and in particular low clouds, reflect solar radiation back into space, thus increasing the albedo and cooling the climate. On the other hand, the water vapor within the clouds absorbs and re-emits long-wave radiation from the surface and hence warms the planet [see e.g., Schneider, 1972, and references therein, as well as Stephens, 2005, for a recent review].

The warming effect of a decreased cloud cover (resulting in a lower albedo and hence an increase in absorbed solar radiation) on the early atmo-

sphere has been suggested as a possible offset to the faint young Sun as part of a negative feedback loop in which lower temperatures decrease (low-level) cloudiness due to a reduction in convective heating and thus increase the amount of absorbed solar radiation, counteracting the initial cooling [Henderson-Sellers, 1979; Rossow *et al.*, 1982]. This hypothesis has been considered an unlikely solution for the faint young Sun problem for a long time, however, because the early Earth was believed to be even warmer than today (presumably resulting in a higher cloud cover due to increased evaporation and thus higher reflectivity of the atmosphere), although more recent studies indicate a more temperate Archean climate (see the discussion in Section 2.3). In any case, the precise effect of cloud feedback for warming or cooling the early Earth remains uncertain. More recently, Rosing *et al.* [2010] argued that the Archean was characterized by larger cloud droplets and shorter cloud lifetimes, effectively lowering the planetary albedo. Their argument is based on the presumption that the majority of cloud condensation nuclei is composed of biologically produced dimethyl sulfide (DMS, (CH<sub>3</sub>)<sub>2</sub>S) and that DMS is produced by eukaryotes only. Both these assumptions have been challenged, however [Goldblatt and Zahnle, 2011a].

It has been hypothesized that a decrease in the cosmic-ray flux due to the stronger solar wind of the young Sun would decrease cloudiness and thus provide additional warming to early Earth [Shaviv, 2003]. For the present-day climate, the cosmic-ray hypothesis could not be verified using satellite observations of cloud cover, however [e.g., Kristjánsson *et al.*, 2008; Gray *et al.*, 2010].

The most comprehensive assessment of the effects of clouds on the early Earth's climate has recently been undertaken by Goldblatt and Zahnle [2011b]. They find that removing all low clouds (which increase the albedo, but not the greenhouse effect) yields a forcing of  $\Delta F = 25 \text{ W m}^{-2}$  and thus only about half the climate forcing required to offset the faint early Sun ( $\Delta F \approx 60 \text{ W m}^{-2}$  and  $\Delta F \approx 40 \text{ W m}^{-2}$  for the early and late Archean, respectively), while more realistic reductions of low cloud cover result in forcings of  $\Delta F = 10 - 15 \text{ W m}^{-2}$ .

In contrast to a diminished cooling effect of low clouds, a stronger warming due to more thin, high clouds could also contribute to a warming of the Archean atmosphere. Indeed, such an effect has been investigated in the context of climate models of an ozone-free atmosphere [Jenkins, 1995a, b, 1999]. Both photochemical models [Kasting *et al.*, 1979] and the discovery of mass-independent fractionation (MIF) of sulfur isotopes in rocks older than 2.45 Ga [Farquhar *et al.*, 2000]

suggest that the oxygen concentration in the early atmosphere was very low until 2.3–2.4 Ga [Pavlov and Kasting, 2002; Bekker et al., 2004], and the Earth hence lacked an ozone layer. In model experiments, removal of ozone (under present-day boundary conditions) yields a warming of  $2^{\circ}\text{C}$  globally due to an increase in long-wave cloud radiative forcing [Jenkins, 1995a, b, 1999]. The increase in warming in these simulations is due to the lower temperature in the upper troposphere and lower stratosphere, leading to higher relative humidity and thus increased high cloud cover, in particular in higher latitudes.

Rondanelli and Lindzen [2010] focus on the warming effect of high clouds as well, and suggest that thin cirrus clouds in the tropics could be sufficient to offset the low solar luminosity. This hypothesis is based on the ‘iris mechanism’ [Lindzen et al., 2001] suggesting a decrease of tropical cirrus clouds with increasing temperature, effectively a negative feedback in the present-day Earth system. This hypothetical mechanism has been extensively challenged in the literature since no evidence for such an effect could be found in several satellite data sets [Chambers et al., 2002; Fu et al., 2002; Hartmann and Michelsen, 2002; Lin et al., 2002].

Independent of the question whether the Rondanelli and Lindzen [2010] hypothesis appears likely, its effects on the energy balance can be investigated to estimate its potential importance. Similar to their assessment of the warming by a decreased low cloud cover, Goldblatt and Zahnle [2011b] find that compensating for the reduced solar luminosity by enhancing high cloud cover (which adds to the greenhouse effect) is only possible with full cover of high clouds which are unrealistically thick and cold. Offsetting the faint young Sun would require climate forcings of  $\Delta F \approx 60 \text{ W m}^{-2}$  and  $\Delta F \approx 40 \text{ W m}^{-2}$  for the early and late Archean, respectively. High clouds can provide a forcing of  $\Delta F = 50 \text{ W m}^{-2}$  if they cover the whole globe and are made 3.5 times thicker and 14 K colder than conventional wisdom suggests. More realistic forcings from high clouds during the Archean are estimated to be  $15 \text{ W m}^{-2}$  only and thus insufficient to offset the lower solar luminosity [Goldblatt and Zahnle, 2011b].

Hence it appears unlikely that any cloud effect alone can resolve the faint young Sun problem, although their feedback – positive or negative – certainly plays an important role and should be considered in any assessment of the Archean climate. The same is true for other factors influencing the climate on early Earth like its faster rotation and (potentially) smaller continental area.

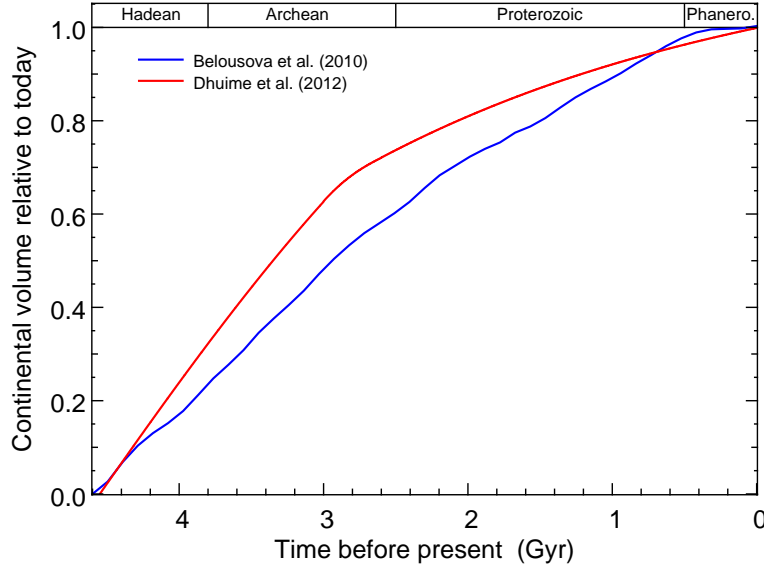
## 7. ROTATIONAL AND CONTINENTAL EFFECTS ON EARLY EARTH

### 7.1. Rotation and Obliquity

In modern times, Earth rotates once every  $\simeq 24$  hours around its axis which is tilted at  $\simeq 23.5^{\circ}$  against the ecliptic (Earth’s orbital plane). Although neither variations of the axial tilt (obliquity) nor of the rotation period directly affect the global energy balance of the climate system, they can, in principle, change the distribution of energy within the system. This has effects for the extent and distribution of ice cover, with consequences for ice-free regions in the oceans, for Earth’s albedo and thus indirectly for the global energy balance.

High obliquity has been shown to yield a warmer climate and could offset the faint early Sun for axial tilt values of  $65 - 70^{\circ}$  in simulations with an atmospheric general circulation coupled to a slab ocean for an idealized supercontinent configuration [Jenkins, 2000]. At high obliquities, the annual insolation at the poles is strongly increased ( $\sim 220 \text{ W m}^{-2}$  for an obliquity of  $70^{\circ}$  and a solar constant reduced by 6%). Although insolation at the equator is lowered by  $\sim 100 \text{ W m}^{-2}$  at the same time, this change in the distribution of insolation is sufficient to prevent early Earth from global glaciation in these simulations. Paleomagnetic studies, however, indicate a remarkable stability of Earth’s (low) obliquity over the last 2.5 Gyr [Evans, 2006], and it has been shown that the presence of the Moon stabilizes the obliquity [Laskar et al., 1993]. Even without the Moon, modeled obliquities remain in a narrow range around the present-day value [Lissauer et al., 2012], suggesting a low obliquity not too different from the present value since the formation of Earth.

Tidal friction causes Earth’s rotation to slow down and the Moon to move further away from Earth over time [e.g., Williams, 2000]. For example, Earth’s rotation period at 4 Ga has been estimated to be just 14 hours [Zahnle and Walker, 1987]. Using a simple one-dimensional (zonally averaged) energy balance model to estimate the effects of a shorter day-length on climate, Kuhn et al. [1989] find that the effect is important for the Precambrian climate since it increases the temperature gradient between equator and poles. This is due to the fact that mid-latitude eddies which are mostly responsible for the heat transport strongly depend on rotation rate: at faster rotation rates, these eddies become smaller in size and thus less efficient in transporting heat polewards. It has been shown that the rate of meridional heat transport is proportional to  $1/f^2$  [Stone, 1972], where  $f = 2\Omega \sin \phi$  is the Coriolis parameter depending on Earth’s rotation rate  $\Omega$  and latitude  $\phi$ . This effect could, in principle, prevent low-latitude glacia-



**Figure 7.** Examples for recent results on the growth of the volume of continental crust over time derived from isotopic data [Belousova et al., 2010; Dhuime et al., 2012].

tion. Note, however, that there is a runaway effect associated with ice-albedo feedback which pushes the planet into a “Snowball Earth” regime once about half of its surface is covered with ice, see the discussion below.

Studies using an atmospheric general circulation model coupled to a simple ocean without heat capacity suggested that fast rotation could decrease global cloud cover by about 20% for a day length of 14 h and thus result in a rise of the global mean air temperature of 2 K [Jenkins et al., 1993; Jenkins, 1993]. In these model experiments, the decrease in cloudiness is due to a weaker Hadley cell and thus reduced convection and cloud formation in equatorial latitudes and larger subsidence in mid-latitudes again reducing cloud cover. A follow-up study with fixed sea-surface temperatures failed to show the effect, however, and found a small increase in global cloud cover [Jenkins, 1996].

Sensitivity studies carried out with atmospheric general circulation models for different rotation periods demonstrate the importance of the rotation rate for the structure and strength of the atmospheric circulation [Williams, 1988; Navarra and Boccaletti, 2002]: with increasing rotation rate, the Hadley and Ferrel cells become generally narrower and weaker, the polar cell tends to split into smaller cells, and the temperature gradient between the poles and the equator increases. How these changes interact with the ocean, however, has still to be demonstrated with fully coupled models using a general-circulation ocean module.

## 7.2. Continental area

A further striking difference between the Archean world and the present-day Earth is the fraction of the surface covered by continents. Dur-

ing the Archean, the land area has been estimated to comprise only about 10% of today’s continental area [Goodwin, 1981]. Earlier models for continental growth yielded widely diverging growth curves for continental volume [see, e.g., Kröner, 1985; Flament, 2009, for an overview], but recent work [Belousova et al., 2010; Dhuime et al., 2012] based on the isotopic composition of zircons provides much better constraints on the evolution of continental volume, which is illustrated in Figure 7. While continental volume has grown to  $\sim 70\%$  by the end of the Archean, it appears likely that a smaller fraction of Earth’s surface was covered by land during the early Archean, which affected both the albedo and heat transport processes in the Earth system.

The lower albedo due to the smaller continental area has been suggested several times as an important factor for the energy budget of the Archean climate [Schatten and Endal, 1982; Cogley and Henderson-Sellers, 1984; Gérard et al., 1992; Jenkins et al., 1993; Molnar and Gutowski, 1995; Ros-ing et al., 2010]. It can be easily shown, however, that the effect of a lower surface albedo alone is insufficient to offset the decrease in solar radiation during the Archean [Walker, 1982; Kuhn et al., 1989]. Goldblatt and Zahnle [2011a] estimate that the decreased surface albedo cannot contribute more than  $5 \text{ W m}^{-2}$  in radiative forcing to any solution of the faint young Sun problem, much less than the values of  $\Delta F \approx 60 \text{ W m}^{-2}$  and  $\Delta F \approx 40 \text{ W m}^{-2}$  required during the early and late Archean, respectively. Despite a decrease in surface albedo, some studies have even suggested an *increase* in global albedo under global-ocean conditions due to higher cloud fractions caused by increased evaporation, although the results strongly

depend on the amount of heat transported from low to high latitudes which has been prescribed in these simulations [Jenkins, 1995a, b, 1999].

In addition to the lower surface albedo, the smaller continental area could have a substantial effect on the heat transport in the Archean oceans and thus the extent of polar ice caps. The influence of meridional heat transport on the latitude of the ice line is illustrated in Figure 8, which is based on results from simple energy balance models and assumptions about albedo changes [Ikeda and Tajika, 1999]. A reduced meridional heat transport indeed results in the ice line being located closer to the equator for a given solar luminosity (or greenhouse-gas concentration) in the stable regime with existing polar caps as indicated by the blue arrow in the Figure. The lower limit in solar luminosity beyond which this stable branch can be occupied, on the other hand, is only slightly affected by meridional transport, see the red arrow in the Figure. Again, these effects would have to be verified with more comprehensive and spatially resolved models to explore the sensitivities of the ice line on geography [Crowley and Baum, 1993], the dynamics of sea ice [Hyde *et al.*, 2000] and ocean dynamics [Poulsen *et al.*, 2001].

Endal and Schatten [1982] suggested that the smaller land fraction in the Archean might have intensified the meridional heat transport in the oceans, thus pushing the boundary of polar ice caps towards higher latitudes. Naively one would expect, however, that the absence of land barriers would lead to a predominantly zonal ocean circulation with reduced heat transport to the polar regions. Indeed, later studies with improved (but still comparatively simple) ocean models found a weak meridional heat transport and thus large temperature gradients between the equator and the poles [Henderson-Sellers and Henderson-Sellers, 1988; Longdoz and François, 1997]. The same behavior was found in simulations with state-of-the-art general circulation models for a planet without any landmass, an “aquaplanet” [Marshall *et al.*, 2007; Enderton and Marshall, 2009; Ferreira *et al.*, 2010].

Note that the extent of exposed continental area and its geographic distribution, where the latter is essentially unknown for the Archean, also affect chemical weathering and thus the carbon cycle [Marshall *et al.*, 1988].

In addition to the rotation rate and the continental distribution, there are other important differences between the Archean and the modern ocean like its possibly higher salinity and increased mixing due to tidal activity, which should be taken into

account in future studies of Archean ocean circulation.

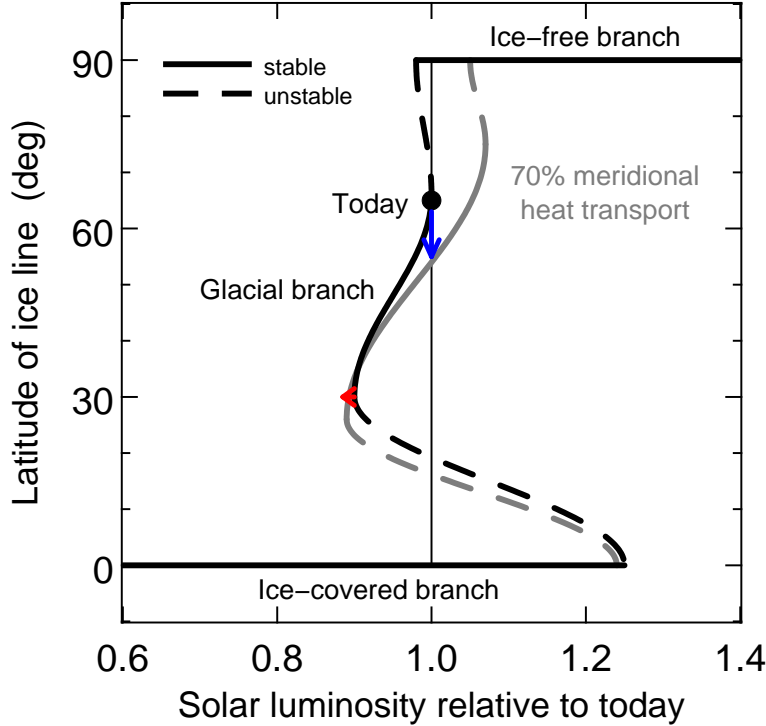
### 7.3. Ocean salinity and tides

Ocean salinity is certainly an important environmental variable, but its evolution over Earth’s history is difficult to reconstruct [Hay *et al.*, 2006]. Based on massive salt beds deposited in more recent times, it has been suggested that the Archean ocean was characterized by a salinity at least a factor of 1.6 higher than today [Knauth, 2005]. In today’s ocean, salinity is dominated by sodium chloride (NaCl), and it is likely that this was also the case in the Archean. Chlorine ( $\text{Cl}^-$ ) outgassed early in the history of life and was dissolved in the earliest ocean [Holland, 1984]. Initial salinity can be estimated from the volume of salt now deposited in massive salt beds and subsurface brines, resulting in salinities up to a factor of 2 higher than today. This appears convincing at least for the early Archean; whether it also holds for the late Archean depends on assumptions about continental evolution during the Archean eon. Unfortunately, geochemical constraints on Archean ocean salinity are currently missing. *de Ronde et al.* [1997] analyzed fluid inclusions in 3.2 Ga deposits interpreted as mid-Archean hydrothermal vents and found chlorine concentrations 1.65 larger than today, but these formations have later been re-interpreted as Quaternary spring deposits [Lowe and Byerly, 2003].

Total ocean salinity is of interest for the Archean climate system because it could in principle influence the thermohaline ocean circulation [Kuhlbrodt *et al.*, 2007]. Indeed, Hay *et al.* [2006] observed that for present-day salinities of  $\simeq 35\%$  the density of seawater changes only weakly with temperature when approaching freezing point, requiring an enhancement of the salt content by sea-ice formation or evaporation to make seawater dense enough to sink to the ocean’s interior. For an ocean with salinities above  $\simeq 40\%$ , the density increases with falling temperature. Therefore, an energy-consuming phase transition during deep-water formation would not be required, which could yield a stronger thermohaline circulation. This claim has been refuted in a modeling experiment by Williams *et al.* [2010], however, which in fact shows a weaker meridional overturning in an ocean model with twice the present-day salinity and today’s topography. The physical reasons for these conflicting assessments of circulation strength for higher average salinity remain unclear, however, and the influence of global salinity on ocean circulation certainly merits further study.

Tidal activity was higher during the Archean due to the smaller orbit of the Moon which affects mixing in the ocean and thus, in turn, ocean





**Figure 8.** Schematic diagram illustrating the position of the ice line as a function of solar luminosity. The positive ice-albedo feedback results in an instability leading to run-away glaciation once the ice line reaches  $\sim 30^\circ$  in latitude. Stable branches are indicated by *solid*, unstable branches by *dashed lines*. The situation for a reduced meridional heat transport is shown in *gray*. The *blue arrow* illustrates the change in the location of the iceline at a given solar luminosity, while the *red arrow* shows the associated change in minimum solar luminosity for the stable glacial branch. Modified after Ikeda and Tajika [1999] and Hoffman and Schrag [2002].

circulation and marine heat transport [Munk and Wunsch, 1998]. Both effects should be explored in more detail with state-of-the-art ocean general circulation models.

#### 7.4. Summary

Rotational and continental effects are thus important for assessing the warming effects on the Archean climate. It is likely that they cannot solve the faint young Sun problem on their own, for which an enhanced greenhouse effect on early Earth appears to be required. The influences of faster rotation and different continental configuration, however, are important for understanding the energy budget and dynamics of the Archean climate system, so any convincing demonstrations of solutions involving enhanced levels of greenhouse gases will require simulations with fully coupled state-of-the-art climate models including these effects.

## 8. CONCLUSIONS AND FUTURE DIRECTIONS

After four decades of research the faint young Sun problem indeed “refuses to go away” [Kasting, 2010]. To a large extent, this is certainly due to the

still limited knowledge of the conditions on early Earth, although the last decades have seen considerable progress, and some parameters are now better constrained than they used to be in the past. Nevertheless, improved constraints on atmospheric composition during the Archean eon would obviously be extremely important, although certainly challenging to obtain. Despite the difficulties involved, there have certainly been remarkable advances in geochemistry in recent years. Note, for example, that most of the geochemical constraints on Archean and Proterozoic carbon dioxide partial pressures shown in Figure 6 were derived within the last decade. There is thus reason to be hopeful in continued progress in this area.

In addition to better data, however, improvements in the efforts on modeling the Earth’s climate during the Archean are urgently needed – as on other important problems in deep-time paleoclimatology like climate changes associated with mass-extinction events [Feulner, 2009] or greenhouse climates of the past [Huber *et al.*, 1999]. Many suggested solutions to the faint young Sun problem, especially those involving continental or albedo effects, require spatially resolved climate simulations rather than the one-dimensional or simple energy balance atmospheric models tradi-



tionally used in studies of the faint young Sun problem, and full coupling to state-of-the-art ocean and sea-ice models. Finally, the full range of feedback mechanisms has to be explored in detail.

There are several challenges in all modeling efforts of the Archean climate. First, there are still considerable uncertainties in key climate characteristics like greenhouse-gas concentrations or continental configuration. These parameter uncertainties have to be properly quantified using ensemble simulations of the Archean climate system. Because of their higher speed, this is traditionally the domain of intermediate-complexity climate models [Claussen *et al.*, 2002].

Secondly, essentially all of the more comprehensive climate models are to some extent tuned to present-day climate conditions. To be able to apply them to the early Earth's climate and obtain meaningful results, they have to provide robust results for a climate state which is considerably different than today. Not only for this reason, the emphasis in all climate modeling efforts for the faint young Sun problem should lie in improving our understanding of the physical processes characterizing the Archean climate system. Finally it would be advisable to simulate the Archean climate with several models using different approaches to be able to compare model results.

Given the continued interest this important topic enjoys, the next decade might bring us closer to finally answering the question of how water on early Earth could have remained liquid under a faint young Sun, certainly one of the most fundamental questions in paleoclimatology.

## GLOSSARY

**Albedo:** Reflectivity of a planet, defined as the ratio of reflected to incoming radiation.

**Anti-greenhouse effect:** Effect of atmospheric gases which are opaque for incoming solar radiation but allow thermal radiation from the surface to escape to space.

**Aquaplanet:** Idealized planet fully covered by an ocean.

**Archean:** Geological eon lasting from  $3.8 \times 10^9$  to  $2.5 \times 10^9$  years ago.

**Banded iron formation:** Sedimentary rock consisting of alternating layers of iron oxides and iron-poor rock.

**Bolometric luminosity:** Luminosity (radiative energy emitted per unit time) integrated over all wavelengths.

**Cosmic rays:** High-energy charged particles (mostly protons, helium and heavier nuclei, electrons) reaching Earth's atmosphere from space.

**Diagenesis:** Sum of all (mostly chemical) low-temperature and low-pressured processes by which sediments are altered after deposition but before conversion to rock (lithification).

**Ecliptic:** Earth's orbital plane.

**Exosphere:** The uppermost layer of Earth's atmosphere.

**Ferrel cells:** Meridional atmospheric circulation pattern between the Hadley and the polar cells.

**Hadean:** Geological eon lasting from the formation of the Earth  $4.56 \times 10^9$  years ago to the beginning of the Archean  $3.8 \times 10^9$  years ago.

**Hadley cells:** Tropical part of the meridional atmospheric circulation, with rising air near the equator, poleward motion in the upper troposphere, sinking air in the subtropics (around  $30^\circ$  latitude in the present-day climate) and a surface flow towards the equator.

**Helioseismology:** Technique to gain insight into the Sun's interior structure from observations of resonant oscillations at the solar surface.

**Hydrothermal vent:** Source of water heated by contact with hot magma in volcanically active areas, commonly used to describe hot springs on the ocean floor.

**Late Heavy Bombardment:** Period of intense collision of asteroids and comets with solar-system planets and moons inferred from a spike in lunar cratering rates  $\sim 3.9 \times 10^9$  years ago.

**Magnetosphere:** Region of interaction between Earth's intrinsic magnetic field and the stream of charged particles from the Sun (the solar wind).

**Main sequence:** Historically identified as a well-defined band in a color-brightness diagram of stars, the main sequence period is the time in the life of a star during which it generates energy by nuclear fusion of hydrogen to helium in its core.

**Mesoproterozoic:** Geological era in the Proterozoic lasting from  $1.6 \times 10^9$  years ago to  $1.0 \times 10^9$  years ago.

**Methanogenic bacteria (methanogens):** Group of anaerobic microorganisms which produce methane.

**Obliquity:** Tilt of Earth's rotation axis against its orbital plane.

**Paleoproterozoic:** Earliest geological era within the Proterozoic eon spanning the time from  $2.5$  to  $1.6 \times 10^9$  years ago.

**Paleosol:** Layer of fossilized soil.

**Photolysis, photodissociation:** Destruction of a chemical compound by photons.

**Planetesimals:** Solid objects with sizes of one kilometer and larger forming in the rotating disk around young stars.

**Polar cells:** High-latitude atmospheric circulation pattern similar to the Hadley cells, with

rising air around 60° latitude in the present-day climate, poleward motion in the upper troposphere, descending air around the poles, and a surface flow towards the equator to close the loop.

**Precambrian:** Informal name for the geological time before the Cambrian, i.e., older than  $542 \times 10^6$  years ago.

**Primordial nucleosynthesis:** Formation of atomic nuclei beyond light hydrogen ( $^1\text{H}$ ) shortly after the big bang, resulting in the production of the stable nuclei of deuterium ( $^2\text{H}$ ), the helium isotopes  $^3\text{He}$  and  $^4\text{He}$  and the lithium isotopes  $^6\text{Li}$  and  $^7\text{Li}$ .

**Proterozoic:** Geological eon lasting from the end of the Archean  $2.5 \times 10^9$  years ago to  $542 \times 10^6$  years ago.

**Protoplanetary disk:** Rotating disk of dense gas and dust surrounding a newly formed star.

**Quaternary:** Geological period spanning the last  $2.6 \times 10^6$  years.

**Radiative forcing:** Change in net irradiance (downwards minus upwards) at the upper limit of the troposphere, thus characterizing changes in the energy budget of the surface-troposphere system.

**Salinity:** Measure of the dissolved salt content of ocean water, usually expressed as parts per thousand.

**Solar analogs:** Stars with physical and chemical characteristics similar to the Sun.

**Solar constant:** Total radiative energy per unit time and unit area incident on a plane perpendicular to the direction to the Sun and at the mean distance between Sun and Earth.

**Solar luminosity:** Radiative energy per unit time emitted by the Sun.

**Solar wind:** Stream of charged particles (mostly electrons and protons) originating in the Sun's upper atmosphere.

**Standard solar model:** Numerical model of the structure and evolution of the Sun based on fundamental equations of stellar physics and constrained by the observed physical and chemical characteristics of the present-day Sun.

**Stromatolites:** Lithified, sedimentary structures growing via sediment trapping by microbial mats.

**Supernatant:** The supernatant water column is the water overlying sedimented material.

**Thermohaline circulation:** Large-scale ocean currents driven by density gradients due to heat and freshwater fluxes at the ocean surface.

**Troposphere:** The lowermost layer of Earth's atmosphere.

**Zero-age main sequence:** Position of stars in a brightness-color diagram which have just

started nuclear fusion of hydrogen to helium in their cores.

## NOTATION

$a$	semi-major axis of Earth's elliptical orbit
$A$	albedo
$\text{CH}_4$	methane
$\text{C}_2\text{H}_6$	ethane
$\text{CaCO}_3$	calcium carbonate
$\text{CaSiO}_3$	wollastonite
$\text{CaSO}_4$	anhydrite
$\text{CaSO}_4 \cdot \text{H}_2\text{O}$	gypsum
$\text{CH}_2\text{O}$	formaldehyde
$(\text{CH}_3)_2\text{S}$	dimethyl sulfide
$\text{Cl}^-$	chlorine
$\text{CO}_2$	carbon dioxide
$\delta^{18}\text{O}$	measure of the ratio of the stable oxygen isotopes $^{18}\text{O}$ and $^{16}\text{O}$
$f$	Coriolis parameter
$\Delta F$	radiative forcing
$\varepsilon$	surface emissivity
$\text{FeCO}_3$	siderite
$\text{Fe}_3\text{O}_4$	magnetite
$G$	gravitational constant
$\text{HCN}$	hydrogen cyanide
$\text{H}_2\text{O}$	water
$\text{H}_2\text{S}$	hydrogen sulfide
$L$	bolometric solar luminosity as a function of time
$L_\odot$	present-day bolometric solar luminosity
$M$	solar mass as a function of time
$\dot{M}$	solar mass-loss rate
$\dot{M}_{\text{fusion}}$	rate of solar mass loss due to nuclear fusion
$\dot{M}_{\text{wind}}$	rate of solar mass loss due to solar wind
$M_\odot$	present-day solar mass
$\text{N}_2$	molecular nitrogen
$\text{NH}_3$	ammonia
$\text{NaCl}$	sodium chloride
$\text{N}_2\text{O}$	nitrous oxide
$\text{O}_2$	molecular oxygen
$\text{OCS}$	carbonyl sulfide
$\text{OH}$	hydroxyl
$\Omega$	Earth's rotation rate
$\Omega_\odot$	solar rotation rate
$\phi$	geographic latitude
$r$	mean distance between Sun and Earth
$R$	radius of the Earth
$S_0$	solar constant
$\sigma$	Stefan-Boltzmann constant

$t$	time
$t_{\odot}$	age of the Sun
$T_s$	surface temperature
$\tau^*$	column infrared gray opacity

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